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CURING AND CHARACTERIZATION OF SILOXANECARBONATE POLYMERS

Danute I. Basiulis
Charles D. Beard
Norman Bilow
Katherine M. Hughes
D. Patrick Salisbury

Hughes Aircraft Company
Advanced Technology Laboratory
Culver City, California

January 1980

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Final Report for Period 27 September 1977 to 21 December 1979

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AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This technical report has been reviewed and is approved for publication.

Harold Rosenberg

HAROLD ROSENBERG
Project Scientists

R. L. VAN DEUSEN, Chief
Polymer Branch

FOR THE COMMANDER

J. M. KELBLE, Chief
Nonmetallic Materials Division

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Glazing interlayers	Aircraft transparencies
Organosilicon polymers	Windshield interlayers
Siloxane polymers	High-temperature interlayers

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Several synthetic procedures were explored to prepare a curable form of the AFML-developed siloxanylenearylene carbonate polymer designated POLYSAC. A method for introducing vinyl groups into the tetrasiloxane portion of the polymer was perfected. Modified curable POLYSAC polymers containing 5, 10, 14, 20, and 30 percent vinyl groups on the tetrasiloxane part of the polymer were synthesized. Several methods of polymerization for achieving high molecular weight were investigated. Condensation (chain extension) of monomers to a molecular weight of up to 11,000 and inherent viscosity of 0.18 dl/g was achieved with

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2, 4, 6-trimethylpyridinium trifluoroacetate as catalyst. The polymer from this process had a yellow color and was transparent. In contrast, inherent viscosities up to 0.38 dl/g were achieved with the HRTTT process. The polymer produced by the latter process was colorless but was somewhat translucent. Curing studies with free radical initiators were conducted on the vinyl-modified POLYSAC. The best cure observed was with dicumyl peroxide as initiating agent. Mechanical tests on cured polymer indicated highest tensile strength from samples cured for two hours at 149°C and postcured for 16 hours at 200°C. Thermal analyses (TGA) on the various modified POLYSAC polymers showed onset of degradation temperatures varying from 375°C to 410°C, with most samples clustering at 380°C. Vinyl content of the polymer was not a significant factor relative to thermal stability. Some synthetic procedures for the polymer were modified resulting in reduced cost. Substitution of a palladium-on-carbon hydrolysis route for silver acetate oxidation is a definite breakthrough in the monomer synthesis process.

FOREWORD

This technical report was prepared by Hughes Aircraft Company, Culver City, California, under USAF Contract F33615-77-C-5163, Project No. 2423, Task No. 242302. The contract was administered under the direction of the Polymer Branch, Air Force Materials Laboratory, with Dr. Harold Rosenberg as Project Scientist.

This report covers work performed from 27 September 1977 to 21 December 1979.

The Hughes program manager was Dr. Norman Bilow, Senior Scientist in the Materials Technology Department. Primary contributors to the laboratory effort were Danute I. Basiulis, Dr. Charles D. Beard and Katherine M. Hughes. Professional assistance was provided by Dr. Richard I. Akawie, Dr. Abraham L. Landis, Seymour S. Schwartz and D. Patrick Salisbury. Professional consultation with Robert H. Johnson is gratefully acknowledged.

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INTRODUCTION

High performance military aircraft require high performance transparencies. These transparencies, used for windshields, canopies, and side windows, are almost always laminates in which two or more load-bearing transparencies are laminated together with an interlayer into a structure which is considerably superior, for the desired application, to a structure of the same thickness of any of the component materials.

The interlayer material used in the new, improved transparencies must meet a particularly strenuous set of requirements. First, the material must be transparent, with a very high degree of luminous transmission and minimum haze. Of equal importance, it must adhere firmly to various types of transparent substrates. There should be a minimum change in the adhesive properties over a temperature range from perhaps as low as -100°C (-150°F) to as high as 180°C (360°F) for the projected Mach 2.5 aircraft. Other requirements which a superior interlayer must meet are minimum degradation after long-term exposure to heat and ultraviolet radiation, as well as thermal and humidity cycling. Degradation is accompanied by loss in tensile strength, change in shear strength and/or adhesive properties, and changes in color or transmission. Another desirable property is flame resistance, or at the minimum, resistance to flame propagation. Also required is sufficient elongation, at all temperatures, to resist bird impact loads, and to absorb the stresses developed by differential coefficients of thermal expansion in the substrate materials.

In short, the interlayer material must at all times, and under all environmental conditions, serve as a transparent bonding agent, transferring loads from one load bearing member to another.

Such a material, POLYSAC, in the form of a base polymer was developed at AFML, but because it was not curable it could not meet all of the requirements. Thus, Hughes Aircraft Company, under sponsorship of AFML, undertook the development of curable modifications of this material. The results of this study are discussed herein.

SECTION II
SUMMARY AND CONCLUSION

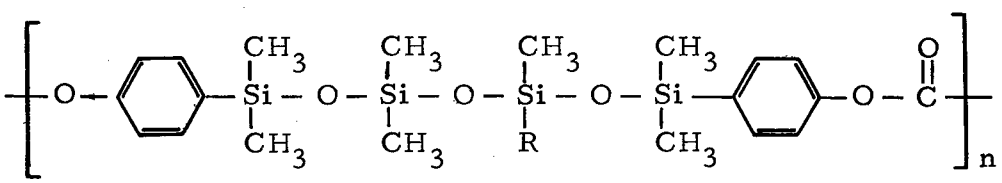
Several synthetic procedures were explored to prepare a curable form of the AFML-developed siloxanylenearylene carbonate polymer designated POLYSAC. A method for introducing vinyl groups into the tetrasiloxane portion of the polymer was perfected. Modified curable POLYSAC polymers containing 5, 10, 14, 20, and 30 percent vinyl groups on the tetrasiloxane part of the polymer were synthesized. Several methods of polymerization for achieving high molecular weight were investigated. Condensation (chain extension) of monomers to a molecular weight of up to 11,000 and inherent viscosity of 0.18 dl/g was achieved with 2,4,6-trimethylpyridinium trifluoroacetate as catalyst. The polymer from this process had a yellow color and was transparent. In contrast, inherent viscosities up to 0.39 dl/g were achieved with the HRTTT process. The polymer produced by the latter process was colorless but was somewhat translucent. Curing studies with free radical initiators were conducted on the vinyl-modified POLYSAC. The best cure observed was with dicumyl peroxide as initiating agent. Mechanical tests on cured polymer indicated highest tensile strength from samples cured for two hours at 149°C and postcured for 16 hours at 200°C. Thermal analyses (TGA) on the various modified POLYSAC polymers showed onset of degradation temperatures varying from 375°C to 410°C, with most samples clustering at 380°C. Vinyl content of the polymer was not a significant factor relative to thermal stability. Some synthetic procedures for the polymer were modified resulting

in reduced cost. Substitution of a palladium-on-carbon hydrolysis route for silver acetate oxidation is a definite breakthrough in the monomer synthesis process. Further development is recommended to cut the number of steps necessary to produce the prepolymer and to achieve a completely transparent, optically clear cured product.

SECTION III
MONOMER SYNTHESIS

The initial approach used in the development of a curable linear polysiloxanylenearylene carbonate is delineated below. Crosslinking was to be accomplished by introducing curing sites onto the polymer chain. This approach would provide processing advantages and maintain the transparency and the high-temperature stability of the elastomer necessary for its use as an interlayer in aircraft windshield and canopy construction.

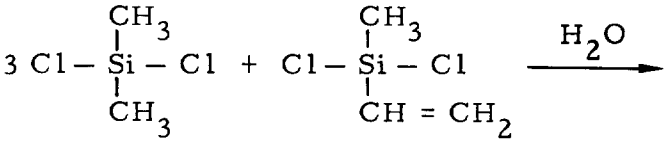
The exploratory development conducted at Hughes to synthesize a curable POLYSAC polymer was based on readily available starting materials such as dichlorodimethylsilane, dichloromethylvinylsilane, p-bromophenol, and diethylamine. The polymer formed from these materials was the vinyl-substituted analogue of the original AFML-developed POLYSAC shown below,

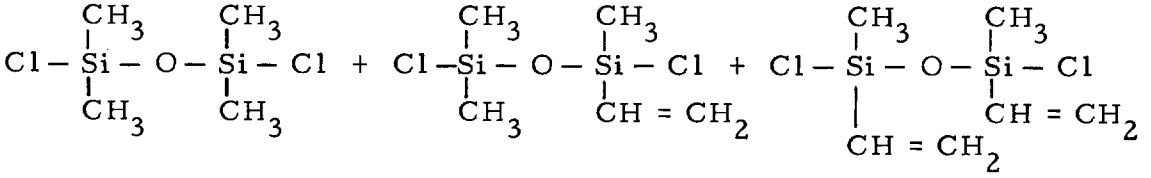


where R can be methyl (CH_3), or occasional vinyl ($CH{=}CH_2$) groups through which the crosslinking can proceed.

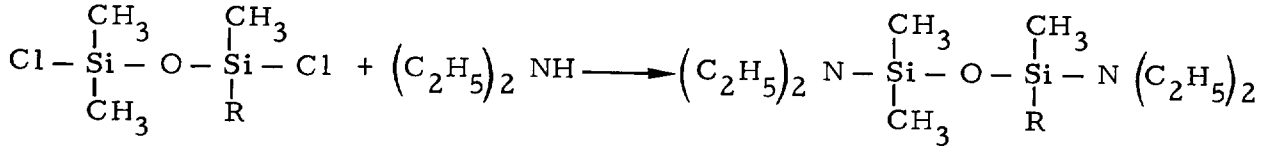
The fundamental approach used was to condense an amine-terminated disiloxane with a phenol-substituted silanol and subsequently to polymerize the resulting bis-phenol to the polycarbonate with phosgene. The polymer was then to be cured through the vinyl groups.

A controlled hydrolysis of a mixture of dichlorodimethylsilane and dichloromethylvinylsilane was carried out by the method of Patnode and Wilcock[1] to give a mixture of disiloxanes.



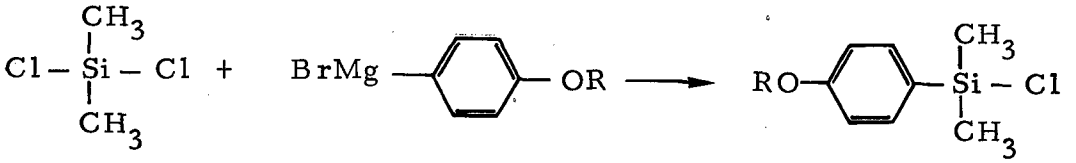


A sixteen percent yield of dimers was isolated and characterized using NMR and infrared spectra. Since the boiling points of the tetramethyl and trimethylvinyl derivatives were expected to be similar, the mixture was to be used as one with a known vinyl concentration and combined with dichlorotetramethyldisiloxane prepared independently by partial hydrolysis of dichlorodimethylsilane. The dichlorodisiloxane derivatives were then to be reacted with diethylamine to prepare the reactive intermediates (disilazanes) shown below.

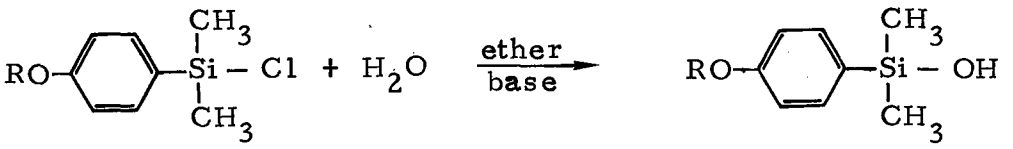


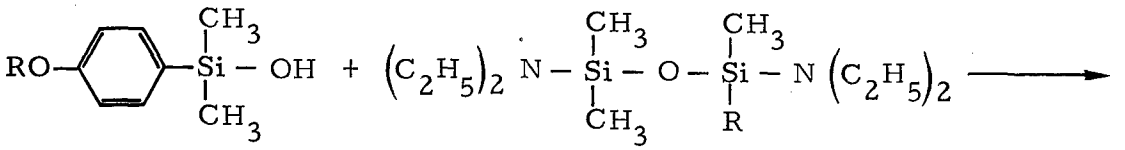
R = CH_3 or $CH=CH_2$

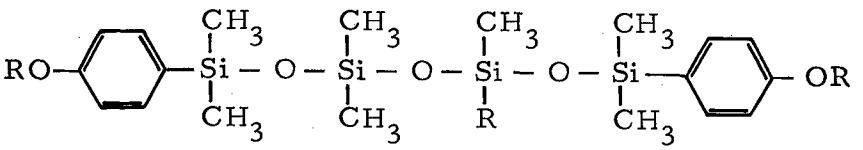
The proposed synthesis sequence which was to be used for the curable POLYSAC preparation is outlined below.



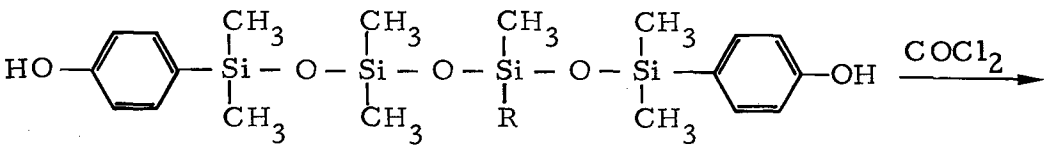
Where: R = protecting group.

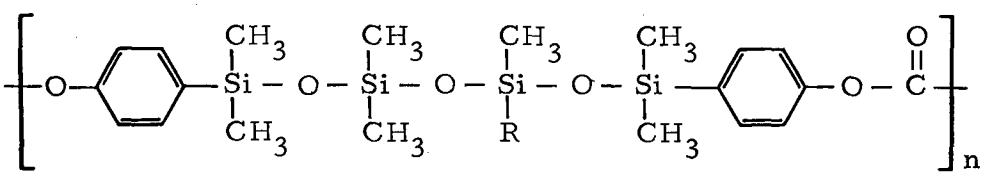






Upon removal of the protecting group, the bisphenol was to have been polymerized with phosgene into the curable POLYSAC.





Protection of the p-bromophenol was smoothly accomplished by etherification[2] with dihydropyran to give up to 93 percent yields of p-bromophenol-2-tetrahydropyranyl ether. The Grignard reagent made from the protected phenol in tetrahydrofuran was added to dichlorodimethylsilane, but the expected product could not be isolated by filtration of the reaction mixture and vacuum distillation of filtrate.

The approach to the synthesis of bis(hydroxyphenyl)octamethyltetrasiloxane was then reconsidered. Octamethylcyclotetrasiloxane was converted to 1,7-dichlorooctamethyltetrasiloxane[3] and subsequently reacted with the 2-tetrahydropyranyl ether of p-hydroxyphenylmagnesium bromide. The acidic workup of the reaction mixture apparently destroyed the product as determined by infrared spectrometry. It was evident that the silicon-phenyl bonds had been cleaved and this conclusion was supported by the prior work of Speier[4]. Isomers which bear oxygen atoms para to the silicon-phenyl bond are particularly sensitive to such cleavage. Evidently, in aqueous solution even a phenolic OH can be acidic enough to promote the cleavage. Studying the matter further, the conclusion was reached that m-bromophenol would be a better starting material. In compounds of the trimethylsilylphenyl type substituted with a methoxy group, the sigma values for the acid catalyzed silicon-phenyl bond cleavage indicate that the para methoxy group hydrolysis rate is 1000 times greater than the hydrolysis rate for the meta methoxy group[5].

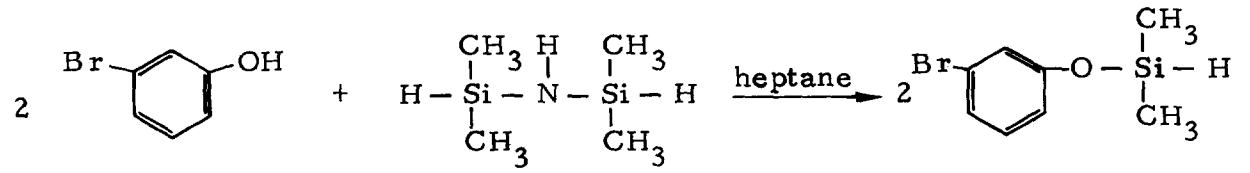
Thus, the 2-tetrahydropyranyl ether of m-bromophenol was prepared and reacted with 1,7-dichlorooctamethyltetrasiloxane via the Grignard reaction. Workup of the reaction product with aqueous ammonium chloride solution kept the molecule intact, but also did not remove the protecting tetrahydropyranyl group. After purification by column chromatography, the protecting group was removed by a hydrolysis catalyzed by p-toluenesulfonic acid. The desired product was not isolated since the severity of conditions necessary to remove the tetrahydropyran protecting group was incompatible with isolation of the 1,7-bis(3-hydroxyphenyl)-octamethyltetrasiloxane.

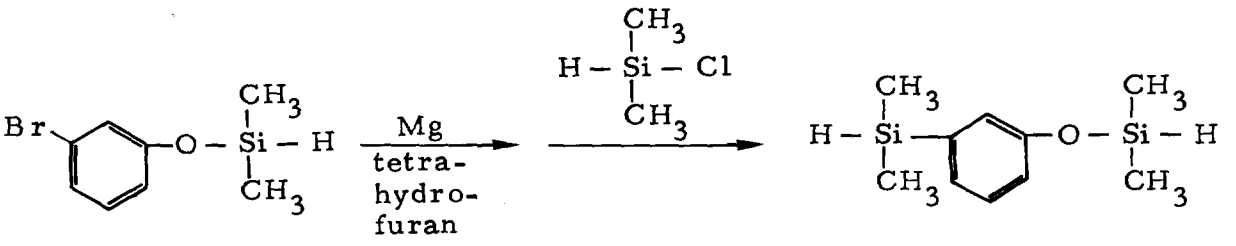
Consequently, another approach was taken. In this approach, the hydroxyl group of p-bromophenol was protected by converting it into its benzyl ether[6] derivative. Subsequently, the 1,7-bis(4-benzyloxyphenyl)octamethyltetrasiloxane was prepared. The benzyl ether protecting group was then removed under neutral conditions by catalytic hydrogenation[7] to give the 1,7-bis(4-hydroxyphenyl)octamethyltetrasiloxane. Since stability of the product under these conditions was questionable, synthesis of the meta isomer, 1,7-bis(3-benzyloxyphenyl)octamethyltetrasiloxane was undertaken. The sensitivity of this compound toward decomposition should be less, because the terminal meta-hydroxyphenylsilyl groups can be expected to hydrolyze at a rate about 1000 times slower than the rate of the para analogue. The hydrogenolysis of the para isomer formed highly impure material, either due to the formation of side products or breakdown of the product itself. The meta isomer, after hydrogenolysis, was purified by silica gel column chromatography. The IR spectra of the product at various stages of the purification indicated the presence of the requisite groups. Further purification of the 1,7-bis(3-hydroxyphenyl)octamethyltetrasiloxane was attempted. A reverse phase chromatographic separation on C18 Bondapac failed to promote separation when methanol or methanol plus 1% water was used as the eluant; however, a thin layer chromatographic separation on silica gel (microporasil), using $CHCl_3$ as the eluent, appeared to be effective. In the latter separation, it was found that about four nonpolar impurities were eluted very rapidly, that one highly polar material adhered tenaciously and would not elute, and that a major component (presumably the desired compound) could be isolated.

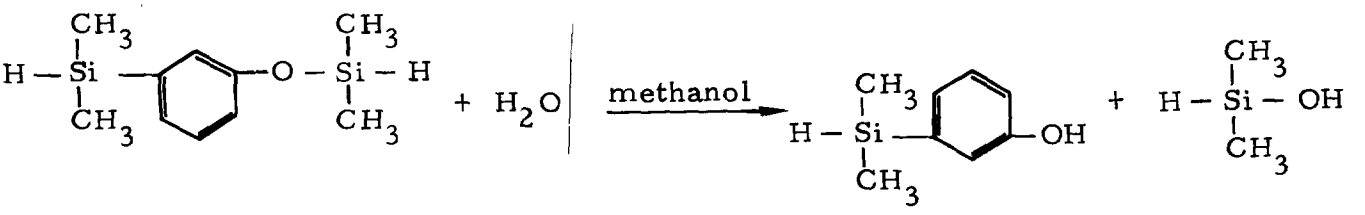
Due to the difficulties encountered up to this point in the approach taken by Hughes, especially in the purification of the synthetic products, and taking into account the work already done inhouse by the Air Force Materials Laboratory and under contract by Midwest Research Institute as reported in their final report of April 1977,[8] it was decided in conjunction with the AFML Project Monitor to terminate the effort on this initial synthetic route. Thus, subsequent work was concentrated on the synthesis of the curable POLYSAC using procedures supplied by Dr. Harold Rosenberg of

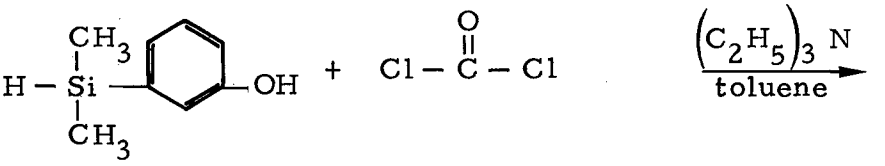
AFML. At this point the curable POLYSAC was to be synthesized from m-bromophenol, because the properties of the meta isomer were superior to those of the compound synthesized from p-bromophenol. This constituted a major change in the program direction.

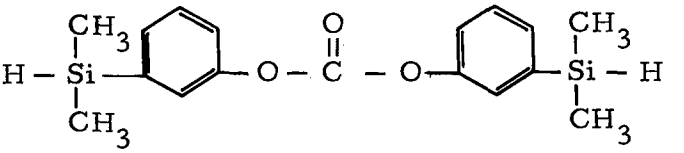
The new approach taken at this point is schematically outlined below.

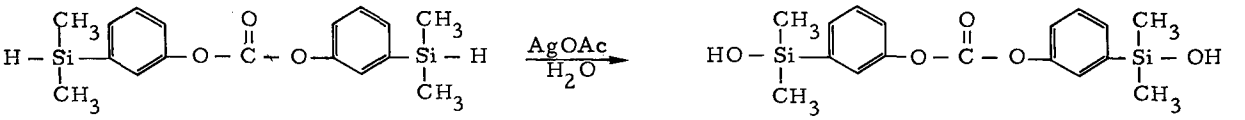




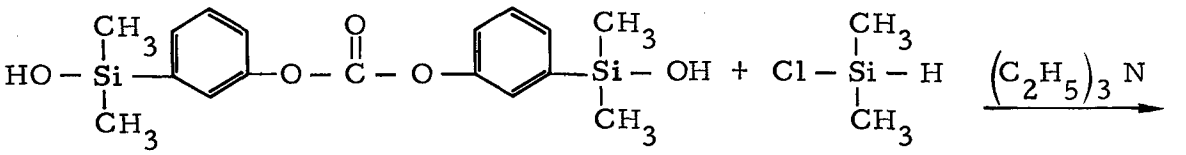


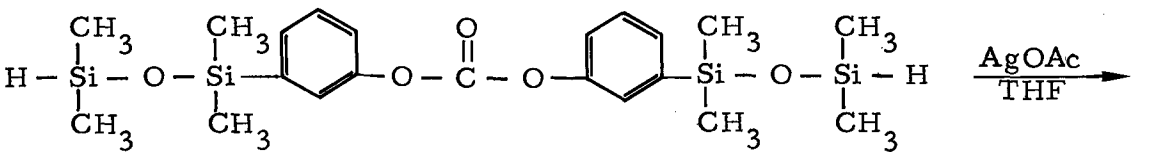


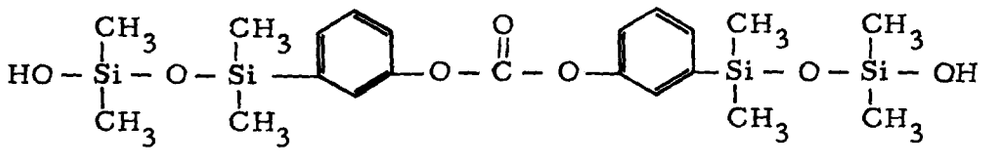


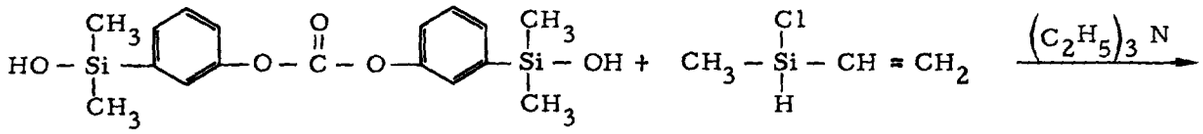


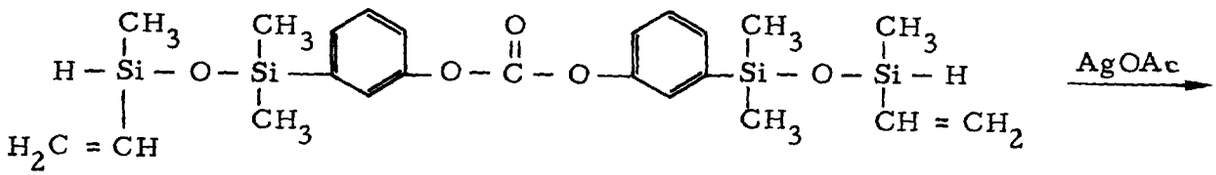
With the bis[3-(hydroxydimethylsilyl)phenyl] carbonate on hand, the cure sites were to be incorporated by reacting the dihydroxy compound with methylvinylchlorosilane and dimethylchlorosilane to give vinylated precursors as shown below.

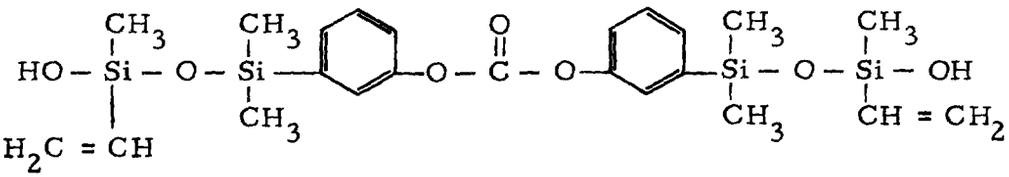












Synthesis of the various intermediates was begun starting with 75 g of 3-bromophenol and progressed smoothly. The 3-bromophenol was first reacted with 1, 1, 3, 3-tetramethyldisilazane to form the 3-bromophenoxydimethylsilane, which was reacted with dimethylchlorosilane via the Grignard reaction. The product, 3-dimethylsilyloxyphenyldimethylsilane, isolated by careful distillation, was then hydrolyzed to the 3-dimethylsilylphenol. Phosgenation of this product proceeded smoothly to the bis[3-(dimethylsilyl)phenyl] carbonate. Silver acetate oxidation of the dihydride resulted in 23 g of bis[3-(hydroxydimethylsilyl)phenyl] carbonate (mp 82°C). The IR and NMR spectra of each compound isolated was compared with the spectra measured at the AFML laboratories. The spectra were in agreement in each case.

For the introduction of vinyl crosslinking sites into the prepolymer, a mixture of 0.05 mole of dimethylchlorosilane and 0.015 mole of methylvinylchlorosilane was reacted with bis[3-(hydroxydimethylsilyl)phenyl] carbonate. The product was distilled under high vacuum to yield 9.0g of a mixture of bis[3-(1, 1, 3, 3-tetramethyldisiloxanyl)phenyl] carbonate, 3-(3-vinyl-1, 1, 3-trimethylsiloxanyl)phenyl 3-(1, 1, 3, 3-tetramethylsiloxanyl)-phenyl carbonate and bis[3-(3-vinyl-1, 1, 3-trimethylsiloxanyl)phenyl] carbonate. Five fractions, boiling at 165°C (30 microns) to 189°C (100 microns), were collected from the distillation. Each fraction was analyzed by IR and NMR. The IR spectra were identical, while the NMR spectra showed a varying vinyl content over a range of 10 to 20 percent. The average was calculated to be 14 percent. The fractions were combined and oxidized with silver acetate and water. The product of this reaction was then used in polymerization studies, which will be discussed later.

Scale-up of the reactions which had worked very well on the first run-through presented a large number of problems. These became apparent with the first large-scale phosgenation. In the scale up, 196 g of 3-dimethylsilylphenol was reacted to yield 28 g (13%) of bis [3-(dimethylsilyl)phenyl carbonate and a large amount of diphenyl carbonate as well

as 3-(dimethylsilyl)phenyl phenyl carbonate. These results placed the focus on the hydrolysis reaction. Formation of 3-dimethylsilylphenol from 3-(dimethylsilyloxy)phenyldimethylsilane was carried out under very mild conditions and subsequent workup consisted of removal of solvent under vacuum. From the NMR spectra of various hydrolysis reactions, the presence of up to 30 percent phenol was detected in the product. From a mixture such as that, formation of a large quantity of side products such as diphenyl carbonate would be expected. The conclusion drawn at the time, namely that only small-scale hydrolyses (under 50 g) reactions were possible, was supported by the results of a phosgenation reaction on 31 g of 3-(dimethylsilyl)phenol. The yield of carbonate in that reaction was 95 percent. The starting material had come from a small scale (50 g) hydrolysis.

The possibility that thermal decomposition was taking place upon distillation of the phosgenation product (bp 155°C at 75 microns) was discounted after one phosgenation reaction was worked up by column chromatography. The product from the reaction, after washing with water, drying over anhydrous magnesium sulfate, and removal of solvent with a rotary evaporator, was placed on a silica gel column and eluted, starting with 10% benzene:90% hexane, and finishing with 50% benzene:50% hexane (by volume).

The first fractions contained material which was the desired product. A total of 17 g was collected, but again this represented only 12 percent of the theoretical yield. The bis[3-(dimethylsilyl)phenyl] carbonate from this run, upon oxidation with silver acetate, gave a product with a mp of 90-91°C.

Small scale hydrolysis reactions on 50 g of 3-(dimethylsilyloxy)phenyl-dimethylsilane were run and analyzed by NMR. The NMR spectra showed impurities were present. In all these hydrolyses the procedure of the AFML laboratories (Procedure A) was used. Subsequently, an investigation of other hydrolysis procedures was undertaken. In conjunction with this investigation, the starting material was redistilled twice and then a 59 g

portion was used for a slightly modified hydrolysis reaction (Procedure B). The results were very good. The yield was 98 percent of theoretical, IR and NMR spectra showed no extraneous material present, and phosgenation of the product from this hydrolysis gave an 86% yield of the desired carbonate. Another hydrolysis procedure[9] was also tried (Procedure C). In this case, the starting material was the same as that used previously in procedure A, but mixed results were obtained. The silane was added dropwise to a solution of water and acetone. Workup of this reaction mixture gave 83% yield of product, whose IR and NMR spectra looked very good. This material, however, was not reacted with phosgene.

The conclusions that were drawn from these reactions were several. The product of the Grignard reaction, 3-(dimethylsilyloxy)phenyldimethylsilane, must be very carefully purified prior to the hydrolysis reaction, since purification of the hydrolysis product is not possible as yet. The hydrolysis procedure preferred is procedure B. In procedure B the methanol and water are mixed first and an exotherm takes place. After cooling the solvent medium, the silane is added dropwise without any other exotherm occurring. Therefore the increase in temperature which may cause a rearrangement does not take place. In procedure A the exotherm of mixing occurs with all reactants present, with the possibility of rearrangement existing. No conclusions were drawn as to the feasibility of scaling up this reaction. The largest run was on 63 g of silane and presented no problem.

The silver acetate oxidation of bis[3-(dimethylsilyl)phenyl] carbonate presented yet another hurdle to scale-up of the reaction procedures. A communication from AFML had suggested that only small scale (~30 g) oxidations should be undertaken. In all, about ten silver acetate oxidations were run on amounts of starting material of up to 28 g. The yields on these oxidations were sometimes as low as 33% and as high as 94%, averaging 71%. Most of these oxidations gave around 70% yield. The melting point of the bis[3-(hydroxydimethylsilyl)phenyl] carbonate was usually 89-90°C. However,

stoichiometric or greater amounts of silver acetate, as well as relatively long reaction times, were required. In addition, attempts to scale-up the reactions sometimes resulted in reduced yields and the product obtained was difficult to isolate and purify. In particular, the work-up was tedious and extensive washing of the organic layer with water was necessary to remove the last traces of acetic acid.

Subsequently, a palladium-on-carbon-catalyzed hydrolysis of the disilanes was developed based on the procedure described by Patterson and Morris[10]. Thus, the disilane was dissolved in tetrahydrofuran and a buffered aqueous solution (pH 7.0), and a 5% palladium on carbon catalyst was added. The reaction mixture was heated at reflux until gas evolution ceased (~1 hr), cooled to room temperature, and the product was readily isolated using a conventional work-up. In numerous experiments the yields were nearly quantitative and the product purity was excellent as judged by NMR and IR.

The disilanols from all the oxidations were used in experiments to determine the optimum amount of vinyl crosslinking sites to be included in the curable POLYSAC prepolymer. The first batch, as already discussed, contained on the average 14 percent vinyl groups. Subsequent runs provided material containing 10, 25, and 30 percent vinyl groups on the siloxane chain. All of these were oxidized using the silver acetate procedure to form the precursor for curable POLYSAC. The disilanol obtained at this stage was not purified beyond drying and removal of residual solvent prior to polymerization experiments.

An alternate route for inclusion of vinyl groups that would provide purer starting materials and better control of the vinyl group content was also investigated. This approach was to make two separate components: bis[3-(3-hydroxy-1,1,3,3-tetramethyldisiloxanyl)phenyl] carbonate (I) and bis[3-(3-hydroxy-3-vinyl-1,1,3-trimethyldisiloxanyl)phenyl] carbonate (II). Then compounds I and II would be copolymerized in the proportions required for best results. Compound I was prepared from the reaction of

bis[3-(hydroxydimethylsilyl)phenyl] carbonate and dimethylchlorosilane, followed by oxidation with palladium on carbon. Compound II was prepared similarly using methylvinylsilane and oxidation with silver acetate. When the palladium on carbon procedure was evaluated for the divinyl analogue, the product obtained consisted largely of the saturated derivative of II, suggesting that hydrogenation of the vinyl group by hydrogen evolved during the ≡ Si-H hydrolysis reaction occurred either before or after hydrolysis, presumably due to hydrogen adsorbed on the catalyst. Thus, the addition of various alkenes directly into the reaction mixture to act as scavengers for hydrogen was investigated. The ratio of vinyl to ether groups (NMR) in the absence of added alkene was 0.10 but repetition of the reaction in the presence of excess isoprene gave a vinyl to ethyl ratio of 1.5; and of 4.0 using 1,4-cyclooctadiene. The experiments were based on readily available olefins and no attempts to optimize the reaction conditions were made. Nonetheless, contingent on the selection of a suitable alkene and further process development, the palladium catalysis reaction appears promising.

In summary, the palladium-catalyzed hydrolysis of both unvinylated disilanes in buffered aqueous tetrahydrofuran solution is a significant improvement in the POLYSAC monomer synthesis sequence. Significant cost reduction and enhanced scale-up potential can be assured.

As discussed above, the palladium-catalyzed hydrolysis of vinyl-containing disilane produces a mixture of products in which much of the vinyl is reduced and thus is not satisfactory for conversion of the divinyl disilane to the disilanol II. Therefore, treatment of the divinyl disilane with an excess of silver acetate in tetrahydrofuran is necessary to give the corresponding disilanol in excellent yield. Removal of excess acetic acid was greatly simplified by washing the organic layer with a buffered aqueous solution. The scale-up potential of this reaction has not yet been defined, however.

SECTION IV
POLYMER DEVELOPMENT

A. POLYMER SYNTHESIS

Initial polymerization studies to find a catalyst for chain extension were conducted on the material containing 14 percent vinyl groups using 1% and 10% acetic acid, as well as 1%, 5%, and 10% tetramethylguanidine. The first results indicated that the tetramethylguanidine did effect polymerization. Another trial with 0.34 N hydrochloric acid resulted in little chain extension taking place.

Merker, et al [11], have used amine salts very effectively in the chain extension of silanols. Amine salt catalysts tried in our research were 2 percent tetramethylammonium bromide, 6 percent tetramethylguanidine heptanoate, 2.7 percent trimethylpyridinium trifluoroacetate, 2.1 percent tetraethylammonium chloride and 2.0 percent trimethylpyridinium acetate. After extended heating periods, both of the trimethylpyridinium salt-catalyzed samples had polymerized to the point that virtually no flow could be observed at 75°C. The trifluoroacetate salt seemed to be the better of these catalysts.

Chain extension studies with 2,4,6-trimethylpyridinium trifluoroacetate (III were continued and are summarized in Table 1. The prepolymer in these studies were material containing 20 percent vinyl moieties (POLYSAC-20), as determined from NMR spectra. From these preliminary tests, the inclusion of 1 percent catalyst and heating for 24 hours under an inert atmosphere at 100-105°C led to the best results. A larger sample, 8.8 g,

TABLE 1. POLYMERIZATION STUDIES OF POLYSAC-20 PREPOLYMER IN AN ARGON ATMOSPHERE WITH 2,4,6-TRIMETHYLPYRIDINIUM TRIFLUOROACETATE AS CATALYST

Sample No.	Catalyst Wt. %	Temp, °C	Time, Hrs	Observations
1	1.2	40	24	Only slight increase in viscosity
2	2.8	40	24	Only slight increase in viscosity
3	3.8	40	24	Only slight increase in viscosity
4	1.1	70	24	Considerable viscosity, clear
5	2.6	70	24	Considerable viscosity, clear
6	4.1	70	24	More viscous than 1, 2 and 3 but less than 4 and 5
7	1.3	100	24	Much more viscous than samples 4, 5, and 6, clear
8	2.7	100	24	Much more viscous than samples 4, 5, and 6, clear
9	4.0	100	24	Viscosity comparable to 6, much less viscous than 7 and 8

was chain extended with 1.02% of the catalyst III for a total of 40 hours at 105°C. The sample was clear and slightly yellowish. The catalyst was washed out from a benzene solution of the sample with water. A total of 7.0 g of polymer was recovered.

B. CURE STUDIES

In the earliest curing studies, conducted on the last sample described in Section A (summarized in Table 2), benzoly peroxide was the most effective curing agent of the three tested. Lauroly peroxide was effective to some extent, while di-tertiary-butyl peroxide had no effect.

Determination of the optimum vinyl content was continued with preparation of 10.8 g of a ten percent* vinylated POLYSAC (POLYSAC-10) and 11.0 g of a thirty percent* vinylated POLYSAC (POLYSAC-30).

POLYSAC-10 was chain extended with 1.6% by weight of catalyst III, with heating for 26 hours under an inert atmosphere. The molecular weight of the product, measured by vapor phase osmometry, was over 7000. POLYSAC-30 was chain extended with 1.5% by weight of catalyst III, with heating for 24 hours. Its molecular weight was 8900. Another sample of POLYSAC-30, chain extended with 1.4% catalyst by weight, had a molecular weight of 11,000. The molecular weights of various samples were summarized in Table 3. Cure studies conducted on POLYSAC-10 and POLYSAC-30 are summarized in Tables 4 and 5. From the results in the tables, it is evident that dicumyl peroxide gave the best results. Of all the peroxides studied, di-tert-butyl peroxide, 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane, bis[α-(tert-butylperoxy)isopropyl] benzene, and lauroyl peroxide were not satisfactory, probably because of their relatively low degradation temperatures.

Another batch of POLYSAC-30 was made and after chain extension, the molecular weight was 7600. Two gram samples of this material were mixed with dicumyl peroxide (3% by weight) by blending in toluene. The sample was cast in a mold 0.060" x 1.0" x 1.5" under argon to be cured as a film.

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*Percentages indicated refer to the % of methyl groups which were replaced by vinyl.

TABLE 2. CURE STUDIES UNDER ARGON ON CHAIN EXTENDED POLYSAC-20

Sample No.	Catalyst Wt. %	Temp, °C	Time, Hrs	Observations
1	2% di-tert-butyl peroxide	120	6-1/2	Not crosslinked
2	4% di-tert-butyl peroxide	120	6-1/2	Not crosslinked
3	2% benzoyl peroxide	70 100	6 16	Slight yellowing, crosslinked
4	4% benzoyl peroxide	70 100	6 16	Slight yellowing, crosslinked
5	2% lauroyl peroxide	65 85	6 16	No change in color. Cross-linked, but softer than 3 and 4
6	4% lauroyl peroxide	65 85	6 16	No change in color. Cross-linked, but softer than 3 and 4

TABLE 3. SUMMARY OF MOLECULAR WEIGHTS OF UNCURED POLYMERS

Notebook #	Vinyl Content, %	Catalyst Wt. %	Time, Hrs	Temp, °C	Prepolymer Molecular Weight
J2332-42	10	1.6	26	100	7000
J2332-21A	20	1.3	24	100	6300
J2332-21A	20	4.0	24	100	4000
J2332-39A	30	1.5	24	100	8900
J2332-44	30	1.4	24	100	11,000
J2332-59	30	1.6	30	100	7600

*2,4,6-Trimethylpyridinium Trifluoroacetate

TABLE 4. CURE STUDIES ON 10% VINYL-CONTAINING CHAIN EXTENDED POLYMER (POLYSAC-10) UNDER ARGON

Sample	Catalyst	Catalyst Wt. %	Temp, °C	Time, Hrs	Observations
1	2,5-Dimethyl-2,5-bis(tert-butylperoxy)hexane	1.1	120	19	Not much change
2	2,5-Dimethyl-2,5-bis(tert-butylperoxy)hexane	3.1	120	19	Not much change
3	Bis[α-(tert-butylperoxy) isopropyl] benzene	1.1	120	19	Solid, elastomeric
4	Bis[α-(tert-butylperoxy) isopropyl] benzene	3.0	120	24	Not much change
5	Dicumyl Peroxide	1.1	120	19	Solid, elastomeric
6	Dicumyl Peroxide	3.1	120	19	Solid, elastomeric
7	Lauroyl Peroxide	1.1	66 followed by 103	7 17	Not much change
8	Lauroyl Peroxide	3.0	66 followed by 103	7 17	Soft, tacky
9	Benzoyl Peroxide	1.0	70 followed by 105	18 6	Soft, tacky
10	Benzoyl Peroxide	3.0	70 followed by 105	18 6	Solid, elastomeric

TABLE 5. CURE STUDIES ON 30% VINYL-CONTAINING CHAIN-EXTENDED POLYMER (POLYSAC-30) UNDER ARGON

Sample	Catalyst	Catalyst Wt. %	Temp, °C	Time, Hrs	Observations
1	2,5-Dimethyl-2,5-bis(tert-butylperoxy)hexane	1.1	120	19	Solid, elastomeric
2	2,5-Dimethyl-2,5-bis(tert-butylperoxy)hexane	3.1	120	19	Solid, elastomeric
3	Bis[α-(tert-butylperoxy) isopropyl] benzene	1.1	120	19	Soft, elastomeric
4	Bis[α-(tert-butylperoxy) isopropyl] benzene	3.1	120	24	Hard, elastomeric
5	Dicumyl Peroxide	1.0	120	24	Solid, some elasticity
6	Dicumyl Peroxide	3.0	120	24	Solid, some elasticity
7	Lauroyl Peroxide	1.0	66 | 7 followed by 103 | 17		Soft, tacky
8	Lauroyl Peroxide	3.0	66 | 7 followed by 103 | 17		Soft, tacky
9	Benzoyl Peroxide	1.0	70 | 2 followed by 105 | 22		Solid, some elasticity
10	Benzoyl Peroxide	3.0	70 | 2 followed by 105 | 22		Solid, some elasticity

The toluene was removed under vacuum with heating up to 115°C. Curing did not take place and the sample had to be reformulated with fresh catalyst (3% by weight). The sample was again heated to 115°C under argon. Curing finally was effected. Some oxygen inhibition was noted. The cured samples were subsequently and gradually heated to 250°C to postcure them.

C. MECHANICAL TESTS

The cured elastomer was tested as to its mechanical properties. A batch of POLYSAC-30 was blended on a mini-mill with 3.3% dicumyl peroxide. The catalyzed material then was cast in a mold under an argon atmosphere. After two hours at 149°C (300°F) the cured product was almost tack-free, a condition in which it could be expected to be applied as an interlayer material. The postcure conditions and tests run on dogbone specimens are summarized in Table 6. All tensile strengths for J2332-89 were 14-57 percent greater than those observed for J2332-59. In contrast, all elongation values were lower (16-20% vs. 140%). The J2332-89 samples thus are much more highly crosslinked. Lower vinyl contents would thus be preferred.

D. THERMAL ANALYSES

Samples of curable POLYSAC were subjected to thermomechanical analyses to determine the onset of degradation temperature. The first sample that was investigated was one consisting of material that had been combined from two trial chain extensions. The chain extensions had been run on prepolymer with 14 percent vinyl content. One portion had been catalyzed with 2.7 percent trimethylpyridinium trifluoroacetate (III) and another with 2.0 percent trimethylpyridinium acetate. After removal of catalyst from the polymer and curing with 3.0 percent benzoyl peroxide at 75° for three days, the curing temperature was gradually increased to 105°C over a 24-hour period. Thermogravimetric analysis of this sample (Figure 1) indicates the onset of degradation occurring at 375°C.

TABLE 6. POLYSAC-30 MECHANICAL TESTS*

Notebook Number	Number of Samples	Postcure Conditions	Tensile Strength, psi	Elongation, %	Elastic Modulus, psi
J2332-59	5	4 hours at 115°C, then 5 hours at 200°C, then 1 hour at 250°C	28.4	140	15.9
J2332-89	5	18 hours at 149°C	32	16	
J2332-89	3	2 hours at 149°C 16 hours at 200°C	44	16	
J2332-89	2	2 hours at 149°C 16 hours at 177°C	34	20	

*Note that these values were measured on polymer which in no way was considered to have an optimum cure. The small amount of material available greatly restricted the number of cure tests that could be performed.

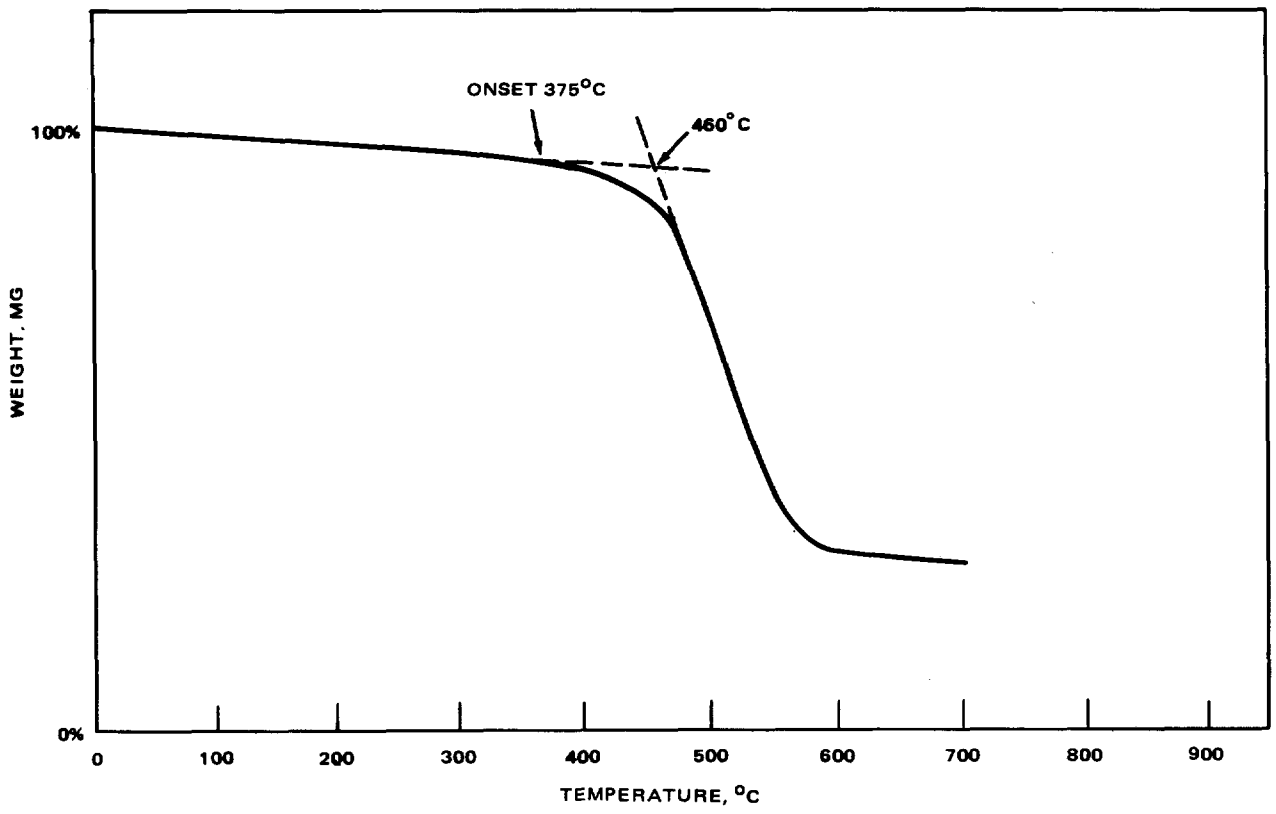

Figure 1. Thermogravimetric analysis of cured POLYSAC-14.

Another sample, POLYSAC-20, which had been chain extended using 2,4,6-trimethylpyridinium trifluoroacetate and subsequently cured with 4 percent benzoyl peroxide showed an onset of degradation at 325°C and an extrapolated degradation temperature of 418°C (Figure 2).

A POLYSAC-10 sample, also chain-extended with catalyst III and, after work-up, cured with 3 percent dicumyl peroxide, showed onset of degradation at 380°C (Figure 3) and an extrapolated degradation temperature of 455°C. A similar experiment with a sample of POLYSAC-30 which also had been chain-extended with catalyst III and then cured with 3 percent dicumyl peroxide showed onset of degradation occurring at 410°C and an extrapolated degradation temperature of 460°C (Figure 4).

A sample of POLYSAC-10 which had been chain-extended using phosgene (Tsai and Rosenberg (12)), was also tested. The onset of degradation for that sample is again at 370°C with the extrapolated degradation temperature being 400°C (Figure 5).

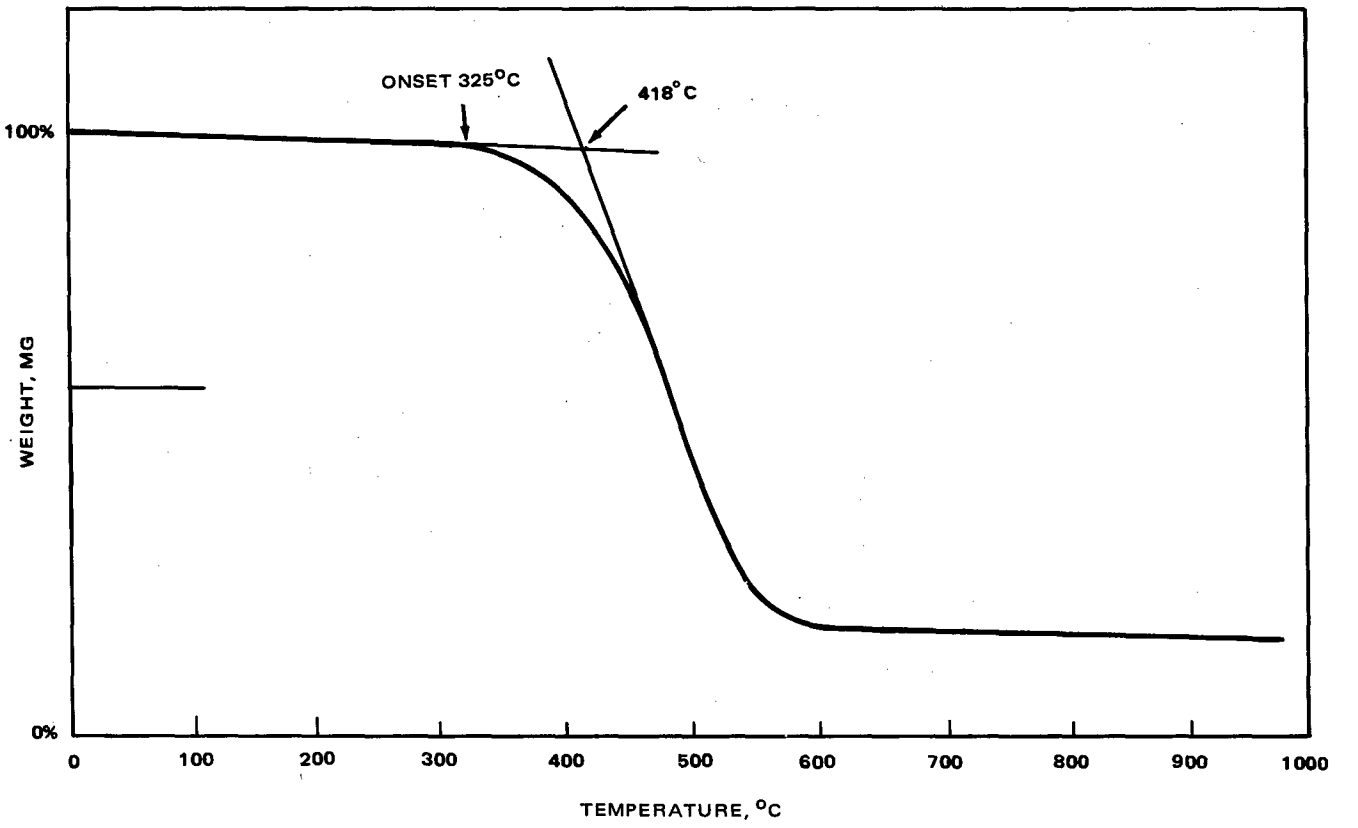

Figure 2. Thermogravimetric analysis of cured POLYSAC-20.

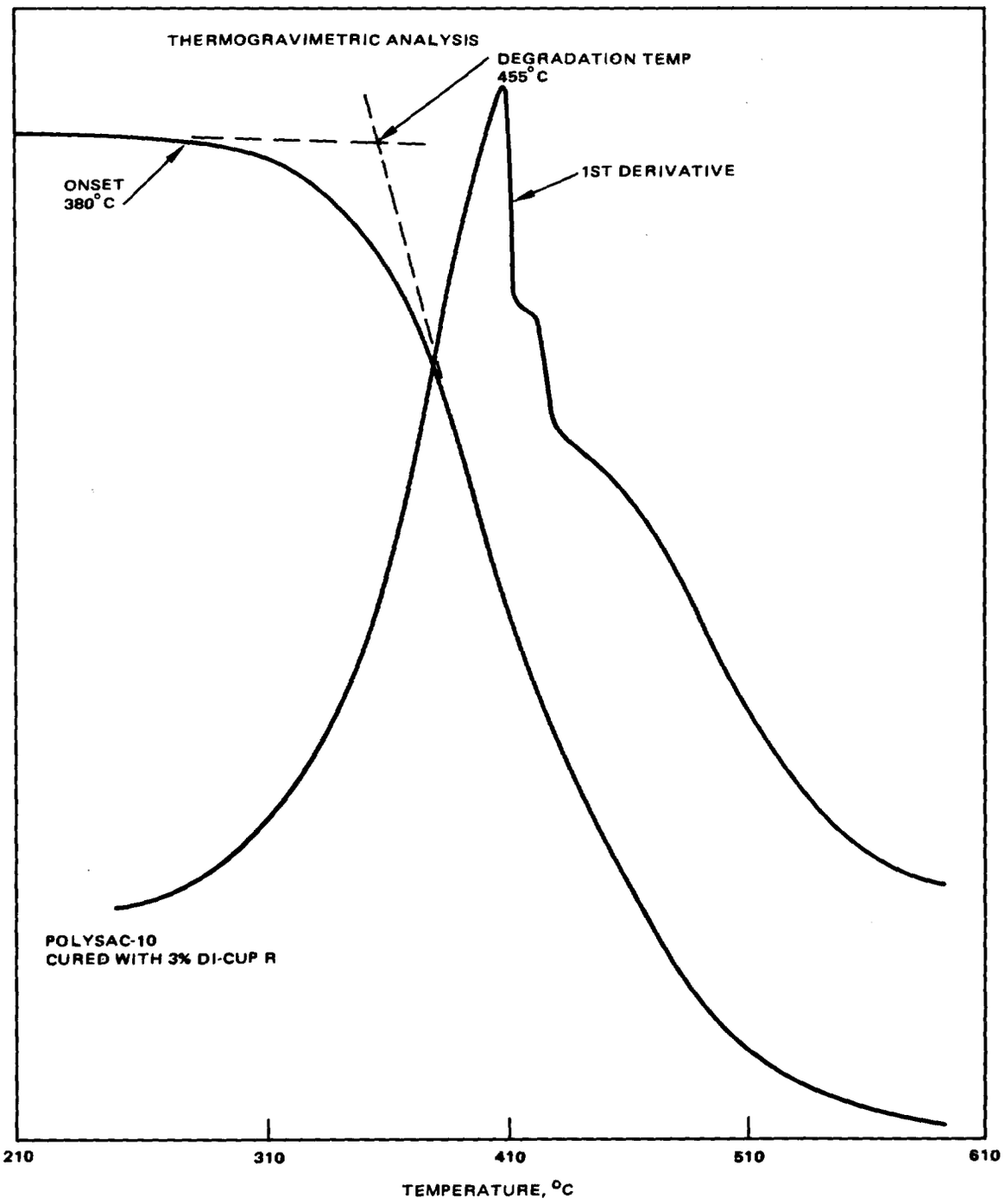

Figure 3. Thermogravimetric analysis of cured POLYSAC-10.

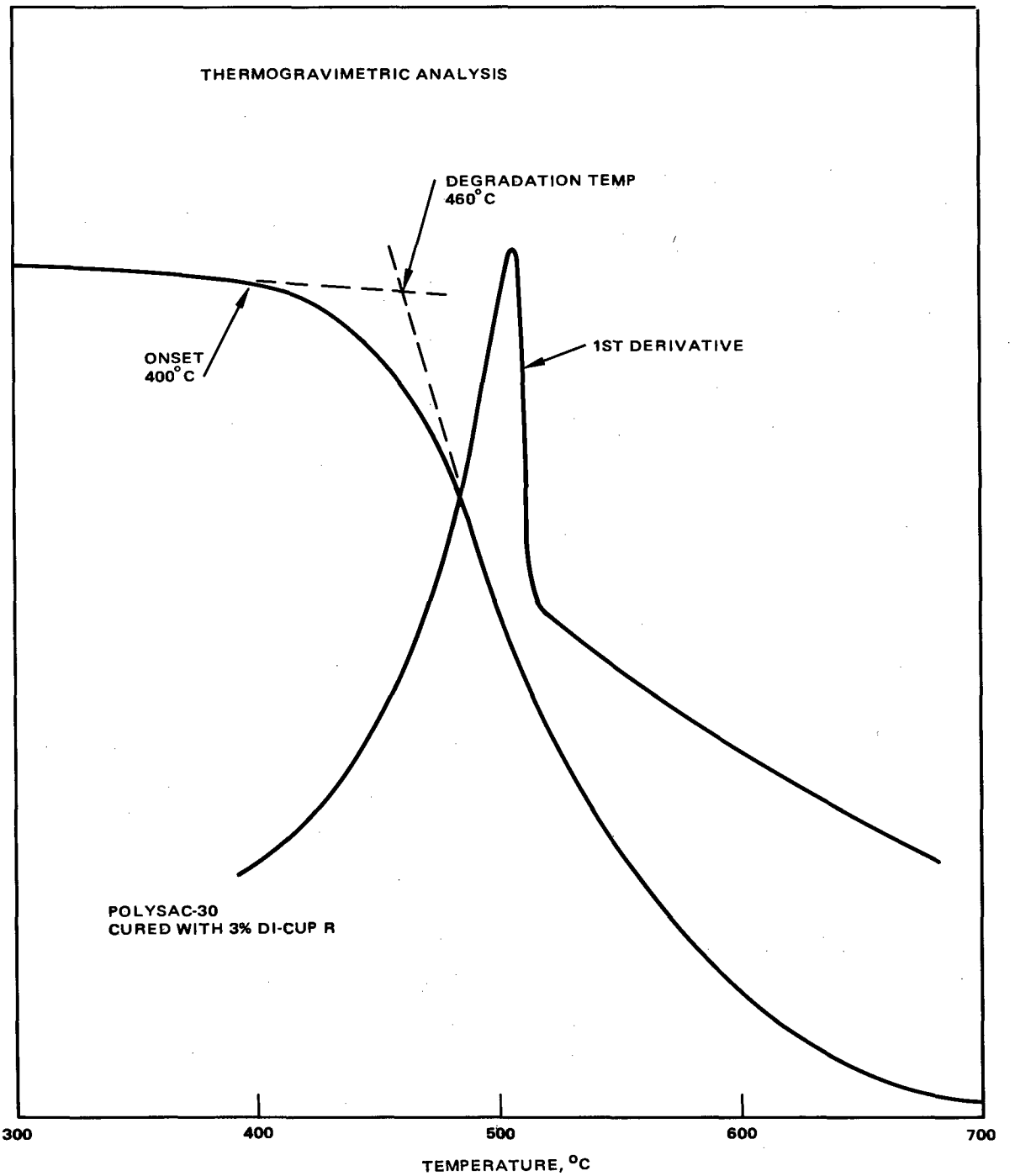

Figure 4. Thermogravimetric analysis of cured POLYSAC-30.

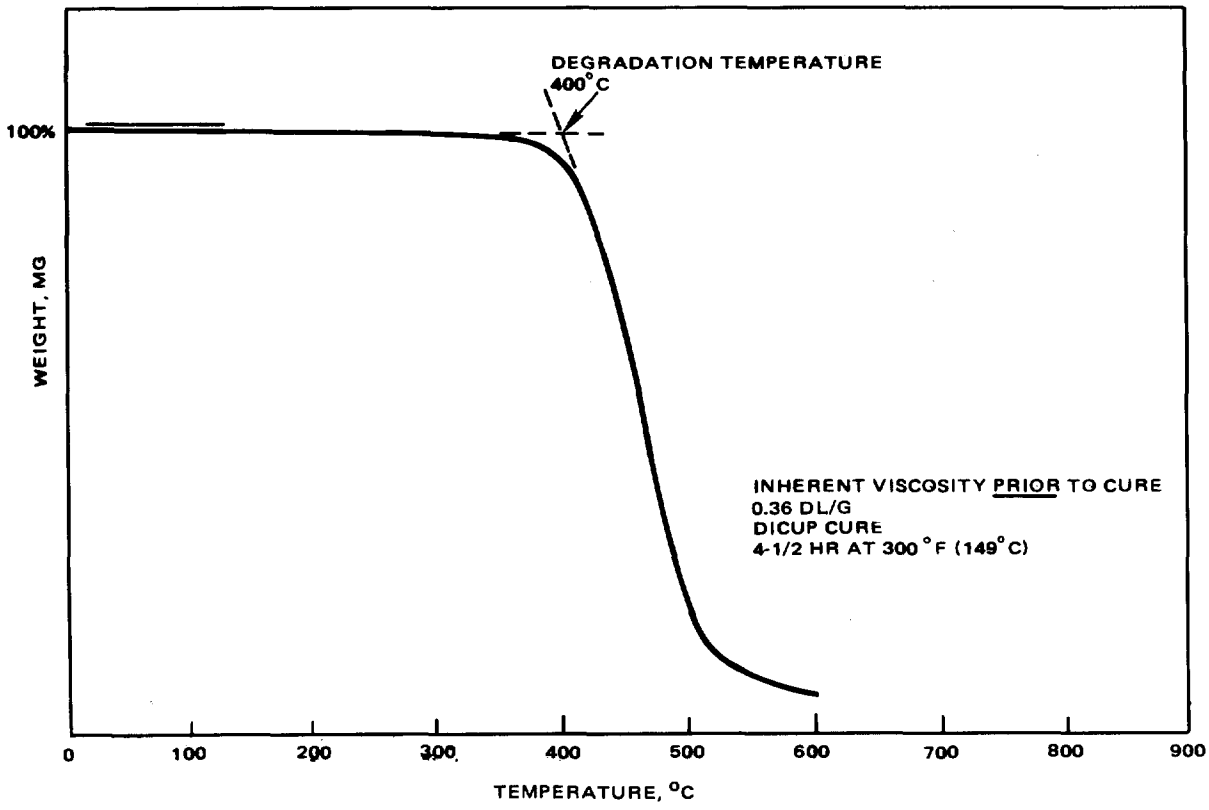

Figure 5. Thermogravimetric analysis of cured POLYSAC-10.

E. ALTERNATE SYNTHESIS OF POLYMERS

All the curable POLYSAC polymers which had been prepared during the course of the contract using 2,4,6-trimethylpyridinium trifluoroacetate had been yellow, were not too high in molecular weight, were not transparent, and were brittle or crumbly in consistency. The recently-developed HR TTT method by Tsai and Rosenberg[12] using phosgene was then used in an effort to eliminate some of the problems.

Catalyst III had been used on the mixed vinyl-methyl precursors where purity of the monomers had been more difficult to establish. With this new method, pure compounds I and II were mixed together and then polymerized. All together four such polymerizations were run and inherent viscosities of the polymers were determined. The results are summarized in Table 7. The inherent viscosities were determined using a Cannon-Fenske viscometer, in dichloromethane, 2.0 g/dl, at 25°C. The first two

TABLE 7. VISCOSITY DATA ON POLYSAC

Notebook No.	Vinyl Content, %	Inherent Viscosity, dl/g
J2749-39	0	0.26
J2749-41	0	0.35
J2749-44	10	0.39
J2749-48	5	0.29
J2332-89	30	0.18

samples contained no vinyl groups. Sample J2749-44 contained five percent of compound II or ten percent of vinyl groups. The material was white, opaque and had the highest inherent (0.39 dl/g) viscosity of all the samples run. Sample J2749-48 with 5 percent vinyl moieties had an inherent viscosity of 0.29 dl/g, but was also white and opaque, as were the first two samples run. The last sample in the table, J2332-89, POLYSAC-30, was polymerized using catalyst III and is included here for comparison of viscosities achieved by the two different methods.

Sample J2749-44 was combined with 3 percent dicumyl peroxide on a mini-mill and cured under argon for four hours at 149°C. At the end of that time, the sample had cured, but was white, translucent, and brittle. The polymer made from this run was chromatographed on a silica gel column and eluted with methylene chloride. The fractions collected were all white and translucent. Another attempt was made to clarify the polymer by fractional precipitation. However, the polymer collected from the different fractions was opaque. At this point the reasons for the translucency cannot be discerned.

The polymerization of prepolymer J2749-48, containing 5 percent vinyl moieties, was followed by NMR over a twenty-three-hour period by observing three areas: a singlet at 0.42 ppm, a singlet at 0.53 ppm and the two superimposed singlets at 0.70 ppm. As the polymerization continued

there were five aliquots taken and analyzed by NMR. The first aliquot was taken after the reaction had progressed for 1/2 hour, the second - 2 hrs and 15 minutes, the third - 4 hours, the fourth - 6 and 1/2 hours, the fifth and final one - 23 hours. The singlet at 0.53 ppm and one of the singlets at 0.70 ppm decreased over the time of the reaction until they were no longer visible at completion of the polymerization. The NMR spectra of the starting materials does not correspond to the singlet observed at 0.53 ppm and one of the singlets at 0.70 ppm. Therefore, those two peaks must correspond to some intermediate that is formed from the interaction of phosgene and the disilanols being polymerized namely compounds I and II.

The polymer that was isolated from this reaction was worked up as before. A thin film of the polymer deposited from methylene chloride on a microscope slide and pressed down with another appears clear.

Translucency of the bulk polymer may at this point be attributed to impurities in the monomers, not sufficiently high molecular weight, or too wide a distribution in molecular weights. More work obviously needs to be done, since there is promise of success as shown by the microscope slide experiment. An examination of the vinylated copolymer under the electron microscope showed no evidence of particulate matter; thus this is not the cause of the observed translucency. Furthermore, polymer produced by the trimethylpyridinium trifluoroacetate-catalyzed telomerization is transparent, although very slightly colored, so translucency does not appear to be an inherent characteristic of the polymer. It is only the polymer made by the Tsai/Rosenberg process that had the translucent appearance, which incidentally could not be eliminated by silica gel chromatography. The Tsai/Rosenberg process thus has the advantage of giving colorless polymer of higher molecular weight than that achieved with the catalysts used previously, but currently has the disadvantage of yielding translucent polymer. Some research is obviously needed to resolve this problem.

SECTION V
EXPERIMENTAL PROCEDURES

Controlled Hydrolysis of Dichlorodimethylsilane and Dichloromethylvinylsilane (J1278-53)

In a 2-l flask were combined under argon 230 ml (1.90 moles) of dimethyldichlorosilane and 81 ml (0.62 mole) of methylvinylchlorosilane together with 500 ml of anhydrous ethyl ether. To the reaction flask was added a solution of 23 ml (1.26 moles) of distilled water in 25 ml dioxane with stirring. Evolution of hydrochloric acid gas took place. The reaction was allowed to sit overnight. The solvents were distilled off and the residue fractionally distilled. The second fraction collected boiled from 134 to 165°C and weighed 83.6 g. This represented about a sixteen percent yield of dimers consisting of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, 1,3-dichloro-1,1,3-trimethyl-3-vinyldisiloxane and 1,3-dichloro-1,3-dimethyl-1,3-divinyldisiloxane.

Formation of 4-Bromophenol 2-Tetrahydropyranyl Ether (J1278-56)

In a one-liter three-neck round bottom flask was placed 48.62 g (0.58 mole) of dihydropyran, freshly distilled from sodium hydroxide pellets. Four drops of concentrated hydrochloric acid were added. The flask was cooled with ice and 50 g (0.29 mole) of 4-bromophenol was added over a two hour period. Two hundred ml of ether were added to the reaction mixture. The mixture was washed with 100 ml of 10% sodium hydroxide solution and the organic layer was dried over anhydrous sodium sulfate. Distillation yielded 64.67 g (87%) of 4-bromophenol 2-tetrahydropyranyl ether boiling at 115°C (700 microns). The reaction was run four times with yields varying from 84 to 94 percent.

Formation of 3-Bromophenol 2-Tetrahydropyranyl Ether (J1278-74)

The procedure was the same as the preceding one. The quantities used were 25 g (0.14 mole) of 3-bromophenol and 51 ml (0.64 mole) of dihydropyran together with two hundred ml of ether for dilution at the completion of reaction. One hundred ml of 10% sodium hydroxide was used to wash the product. Distillation isolated 32.03 g (89%) of product boiling at 100°C (100 microns).

Attempted Preparation of 4-(Chlorodimethylsilyl)phenol (J1278-60) (J1278-64)

In a dry 250-ml three-neck round bottom flask equipped with a mechanical stirrer and paddle, reflux condenser, and argon inlet and outlet were placed 6.68 g (0.25 g-atom) of magnesium and 25 ml of tetrahydrofuran (distilled from lithium aluminum hydride). A pressure-equalizing addition funnel was used to add dropwise 64.64 g (0.25 mole) of 4-bromophenol 2-tetrahydropyranyl ether dissolved in 100 ml of tetrahydrofuran. The reaction was slow to start and had to be initiated with a little iodomethane and heating. When all of the magnesium appeared to have been consumed, the resulting Grignard reagent was added via a double-tipped needle to a three-neck one-liter flask containing 60 ml of freshly-distilled dichlorodimethylsilane with vigorous stirring. Salt formation was immediately visible. The reaction mixture was allowed to sit for two days. The excess tetrahydrofuran and dichloromethylsilane were removed under reduced pressure. The salts were filtered off under argon atmosphere and were washed with xylene. The filtrate was very black. Vacuum distillation of the filtrate was unsuccessful as it all polymerized.

Preparation of 1,7-Dichlorooctamethyltetrasiloxane (J1278-68, 76)

In a one-liter three-neck flask were placed 100 g (0.34 mole) of octamethylcyclotetrasiloxane together with 5 g of triphenylphosphine and

190 ml of thionyl chloride. The reaction mixture was heated at 54-56°C for two hours under an argon atmosphere. Sulfur dioxide was evolved. The reaction mixture was allowed to sit overnight at room temperature. After twenty hours the excess thionyl chloride was distilled off. The product, boiling at 78-80°C (10 mm), was isolated; the yield was 91.28 g (77%) of 1,7-dichlorooctamethyltetrasiloxane.

Attempted Preparation of 1,7-Bis(4-hydroxyphenyl)octamethyltetrasiloxane (J1278-70) (J1278-74)

In a dry 500-ml three-neck round bottom flask, equipped with a mechanical stirrer and a paddle, reflux condenser, and argon inlet and outlet were placed 1.46 g (0.06 g-atom) of magnesium and 15 ml of tetrahydrofuran (distilled from lithium aluminum hydride). To the flask was added dropwise from a pressure-equalizing funnel 15.0 g (0.058 mole) of 4-bromophenol 2-tetrahydropyranyl ether in 20 ml of tetrahydrofuran. The reaction mixture was refluxed for four hours. Then a pressure-equalizing addition funnel was used to add dropwise a solution of 10.0 g 0.028 mole) of 1,7-dichlorooctamethyltetrasiloxane in 20 ml of tetrahydrofuran. Upon completion of the addition the reaction mixture was refluxed for 45 minutes and poured into 150 ml of a solution containing 75 g of ammonium chloride dissolved in 450 ml of water. The organic layer was separated and washed with 100 ml of water. The organic layer was dried overnight over anhydrous sodium sulfate. The drying agent was filtered off and the filtrate was concentrated on a rotary evaporator. The residue was purified by silica gel column chromatography and elution with 1:1 ether:carbon tetrachloride. Fraction 3 contained 5.39 g (0.0085 mole) of 1,7-bis[4(2-tetrahydropyranyloxy)phenyl]octamethyltetrasiloxane, as determined by IR spectrophotometry. Removal of the protecting group was undertaken by refluxing this fraction with 0.2 g of p-toluenesulfonic acid in 20 ml of ethanol. Subsequent workup did not lead to the desired product.

Formation of 4-Bromophenol Benzyl Ether (J1278-77)

In a 500-ml round-bottom flask were mixed 32.87 g (0.19 mole) of 4-bromophenol, 35.92 g (0.21 mole) of benzyl bromide, 28 g (0.20 mole) of potassium carbonate and 50 ml of acetone. The reaction mixture was refluxed for 7 hours. The acetone was removed under reduced pressure and the residue shaken with about 100 ml of water and 100 ml of ether. More water was added to dissolve all solids. The organic layer was separated and washed first with 80 ml of 10% aqueous sodium hydroxide, and then with 100 ml of distilled water. The solution was then dried over calcium chloride for three days. The drying agent was filtered off and the ether was distilled. Vacuum distillation of the residue was necessary to remove residual benzyl bromide and other lower boiling components. The residue was recrystallized from methanol to yield 35.08 g (70%) of 4-bromophenol benzyl ether, mp 60.5 - 61°C.

Formation of 3-Bromophenol Benzyl Ether (J1278-82)

The procedure used was the same as the preceding. The quantities used were 29.76 g (0.17 mole) of 3-bromophenol, 29.42 g (0.17 mole) of benzyl bromide, 24.88 g (0.18 mole) of potassium carbonate, and 50 ml of acetone. The product was distilled to yield 34.66 g boiling at 110-128°C (400 microns). This fraction was then recrystallized from methanol to yield 28.5 g (70%) of 3-bromophenol benzyl ether, mp 61°C.

Attempted Preparation of 1,7-Bis(4-hydroxyphenyl)octamethyltetrasiloxane (J1278-79)

In a dry 500-ml three-neck round bottom flask equipped with a mechanical stirrer and a paddle, reflux condenser, and argon inlet and outlet were placed 2.67 g (0.11 g-atom) of magnesium and 15 ml of tetrahydrofuran (distilled from lithium aluminum hydride). To the flask was added dropwise with a pressure-equalizing funnel 27.6 g (0.10 mole) of 4-bromophenol benzyl ether. The reaction was slow in starting and was

refluxed for six hours. A pressure-equalizing addition funnel was used to add dropwise with vigorous stirring 19.33 g (0.05 mole) of 1,7-dichloro-octamethyltetrasiloxane. The reaction mixture was left to sit for two days. The pale yellow reaction mixture was poured into 250 ml of a solution containing 75 g of ammonium chloride in 450 ml water. The organic layer was separated and washed with 150 ml water. A white solid was observed separating from the ether layer and was filtered off. The filtrate was dried over anhydrous sodium sulfate. After filtration, the solvents were removed on a rotary evaporator. The residue weighed 28.26 g. Infrared spectrophotometry confirmed that the residue was the desired product. One half of the residue (14.13 g) was subjected to hydrogenolysis in ethanol with 0.5 g of 5% palladium on carbon as catalyst. Very little uptake of hydrogen took place due to poisoning of the catalyst. More catalyst was added repeatedly. The ethanol solution was filtered and chromatographed through a silica gel column with 1:1 ether:carbon tetrachloride as eluting solvent. Middle fractions from the column were isolated and subjected to hydrogenolysis once again. The theoretical hydrogen uptake of 14.14 lbs took place. The catalyst was filtered off. The workup of the reaction mixture yielded dark components that exhibited an odor of phenol. Infrared spectrophotometry indicated breakdown of the desired product.

Preparation of 1,7-Bis(3-hydroxyphenyl)octamethyltetrasiloxane (J1580-70A)

The procedure used is the same as the preceding one. The quantities of materials were 30.7 g (0.109 mole) of 3-bromophenol benzyl ether, 2.65 g (0.109 g-atom) of magnesium and 17.5 g (0.05 mole) of 1,7-dichlorooctamethyltetrasiloxane. In the work-up 75 ml of the ammonium chloride solution was used. The product was purified first by elution from a silica gel column with carbon tetrachloride. Subsequent hydrogenolysis with platinum oxide was unsuccessful. Hydrogenolysis with 5% palladium on carbon was then carried out and the isolated product, 13.8 g, was chromatographed on a silica gel column once more. Two fractions were isolated. Reverse phase chromatographic separation on

C18 Bondapac failed to promote separation when methanol or methanol plus 1% water was used as the eluant. A thin layer chromatographic separation on silica gel (microporasil), using chloroform as the eluant, separated the mixture into four nonpolar impurities which were eluted rapidly, a highly polar component which would not move, and a major component which could be isolated.

Preparation of 3-Bromophenoxydimethylsilane (J2749-21)

A dry 3-l three-neck flask was fitted with a mechanical stirrer with a Teflon blade, an argon inlet and a reflux condenser connected to an oil bubbler. In the flask were placed 400 g (2.31 mole) of 3-bromophenol and 1000 ml of heptane dried over molecular sieves. A pressure-equalizing addition funnel with an argon inlet was used to add 164.0 g (1.23 moles) of 1,1,3,3-tetramethyldisilazane over a three-hour period. The solution was stirred continuously under argon until no color change was observed when the outlet argon was bubbled into 1% phenolphthalein solution. The heptane was distilled off at atmospheric pressure under argon. Vacuum distillation of the residue gave 516.4 g (97%) of 3-bromophenoxydimethylsilane, b.p. 64-66°C (1.5 mm). This reaction was run six times with yields ranging from 94 to 98 percent.

IR - Figure 6; NMR - Figure 7 (See Appendix)

Preparation of 3-(Dimethylsilyloxy)phenyldimethylsilane (J2749-22)

A dry 5-l four-neck flask was fitted with a mechanical stirrer with a Teflon blade, thermometer, an argon inlet and a Dewar condenser connected to an oil bubbler. In the flask were placed 34.3 g magnesium (1.41 g-atoms) together with one liter of tetrahydrofuran which had been distilled from lithium aluminum hydride. To this solution was added quickly from a pressure-equalizing funnel 93.2 g (0.99 mole) of dimethylchlorosilane. Then 20 to 30 ml of a mixture of 93.2 g (0.99 mole) of dimethylchlorosilane, 360 ml of tetrahydrofuran (distilled from lithium aluminum hydride) and

261.2 g (1.13 mole) of 3-bromophenoxydimethylsilane was added from a pressure-equalizing funnel to the reaction mixture. Once the reaction had started, the remainder of the reactants was added dropwise over a period of two hours while the temperature was held between 45° and 50°C. The reaction mixture was refluxed overnight under argon. The reaction mixture was cooled to room temperature and 750 ml of petroleum ether (bp 30-60°C, dried over molecular sieves) was added to the mixture. The salts were filtered off under argon atmosphere and washed with petroleum ether. The combined filtrate and washings were concentrated on a rotary evaporator. Periodically the solution was filtered to remove salts that had precipitated. The residue was flash-distilled under vacuum and then redistilled to yield 181.5 g (75%) of 3-dimethylsilyloxyphenyldimethylsilane, bp 48-49°C (0.05 mm). This reaction was run nine times with yields ranging from 56 to 77 percent.

IR - Figure 8; NMR - Figure 9 (See Appendix)

Preparation of 3-Dimethylsilylphenol

Procedure A (J2332-71)

A mixture of 50 g (0.24 mole) of 3-(dimethylsilyloxy)phenyldimethylsilane, 15 g (0.81 mole) of distilled water, and 100 ml of methanol was placed in a 500-ml Erlenmeyer flask and stirred with a magnetic stirring bar overnight. After checking the mixture for completion of reaction by measuring the infrared spectrum of the mixture, the methanol was removed on a rotary evaporator at room temperature. The residue was taken up in 100 ml of toluene and dried over anhydrous magnesium sulfate overnight. The drying agent was filtered off and the salts were washed with toluene. Most of the toluene was removed on a rotary evaporator without heating and the residual toluene was removed under vacuum. The yield was 35.55 g (96%) of 3-dimethylsilylphenol. A total of six runs were made.

Procedure B (J2749-26)

In a 500-ml Erlenmeyer flask were mixed 16.9 g of distilled water and 120 ml of methanol. After the mixture had cooled, there was added dropwise 58.6 g (0.28 mole) of 3-(dimethylsilyloxy)phenyldimethylsilane with vigorous stirring. The reaction mixture was stirred overnight. After checking the mixture for completion of reaction by IR spectrometry, the methanol was removed by rotary evaporator at room temperature. The residue was taken up in 110 ml of toluene and dried overnight over anhydrous magnesium sulfate. The drying agent was filtered and the salts were washed with toluene. The toluene was removed on a rotary evaporator under vacuum. The yield was 40.0 g (93%) of 3-dimethylsilylphenol. In a second run, the yield was 98% of theoretical.

Procedure C (J2749-17)

In a dry 250-ml flask was placed 1.71 g of distilled water and 100 ml of acetone (reagent grade) was added. The solution was stirred vigorously while 10 g (0.05 mole) of 3-(dimethylsilyloxy)phenyldimethylsilane was added dropwise. The reaction mixture was stirred overnight. Anhydrous magnesium sulfate was added and the mixture was stirred for 24 hours longer. The drying agent was removed by filtration. The salts were washed with a little acetone. After subsequent removed of solvent on a rotary evaporator, the yield was 6.3 g (83%) of 3-dimethylsilylphenol.

IR - Figure 10; NMR - Figure 11 (See Appendix)

Preparation of Bis[3-(dimethylsilyl)phenyl] Carbonate (J2749-29)

A solution of 84.9 g (0.56 mole) of 3-dimethylsilylphenol, 65.13 g (0.64 mole) of triethylamine (distilled from phenyl isocyanate) and one liter of toluene (dried over molecular sieves) was introduced into a 5-liter three-neck flask equipped with a mechanical stirrer, a pressure-equalizing addition funnel with an argon inlet and a Dewar condenser. After

purging with argon and cooling the flask with an ice bath, 19.3 ml (0.28 mole) of phosgene dissolved in 200 ml of cold toluene was added dropwise to the reaction mixture. Upon completion of the addition, the mixture was stirred overnight. The salts were filtered off and washed with toluene. The filtrate and washings were then washed six times with 400 ml of distilled water. The organic layer was dried overnight over anhydrous magnesium sulfate. After filtering off and washing the drying agent with toluene, the solvent was removed on a rotary evaporator. The residue was distilled to yield 80.9 g (86%) of bis[3-(dimethylsilyl)phenyl] carbonate boiling at 148°C (250 mm). A total of nine runs were made with yields ranging from 12 to 95 percent.

IR - Figure 12; NMR - Figure 13 (See Appendix)

Preparation of Bis[3-(hydroxydimethylsilyl)phenyl] Carbonate

Procedure A (J2749-32-1)

A solution of 24.0 g (0.073 mole) of bis[3-(dimethylsilyl)phenyl] carbonate, 417 ml of tetrahydrofuran, and 47 ml of distilled water were placed in a 3-liter three-neck flask equipped with a thermometer and a mechanical stirrer. The flask was cooled to -3°C with an ice/salt bath and 27.8 g (0.17 mole) of silver acetate was added in small portions over a four-hour period while stirring the mixture rapidly and not allowing the temperature to rise above 0°C. The reaction was stirred overnight while warming to room temperature. Five hundred ml of benzene was added to the reaction mixture and, after stirring for a short period, the solution was filtered through a fine porosity fritted-glass funnel. The silver salts were washed with 200 ml of benzene. The combined filtrate and washings were washed with saturated sodium chloride solution and the organic layer was dried over anhydrous magnesium sulfate overnight. The salts were filtered off, washed with 200 ml of benzene, and the filtrate was concentrated on a rotary evaporator without heating to a thick oil. Twenty ml of pentane,

dried over molecular sieves, was added to the oil. After a few minutes of shaking, crystals formed. The flask was cooled in ice and the mixture was filtered. Pentane was used to wash the product. Recrystallization from boiling benzene yielded 24.6 g (94%) of bis [3-hydroxydimethylsilyl)-phenyl] carbonate, mp 84-85°C. A second recrystallization yielded 17.4 g, mp 89-90°C. A total of nine runs was made with yields ranging from 33 to 94 percent.

Procedure B (J2749-36)

A 1000-ml three-necked flask was equipped with mechanical stirring, reflux condenser and a heating bath. 5% Palladium on carbon (0.5 g) was added to the reaction vessel, followed by a solution of bis[3-(dimethylsilyl)phenyl] carbonate (39.6 g, 0.120 mole) in 400 ml of tetrahydrofuran and a buffered aqueous solution [80 ml, buffered at pH 7.0 (prepared from 9.1 g KH_2PO_4 and 18.9 g Na_2HPO_4 per liter)]. Gas evolution was observed upon mixing of the reactants, but did not become vigorous until the internal temperature reached 50°C. The reaction mixture was refluxed for 1.5 hr at which time gas evolution was completed. The reaction mixture was cooled to room temperature and filtered. Methylene chloride (800 ml) was added and the resulting mixture was washed thoroughly with water. The organic layer was dried (Na_2SO_4), filtered and the solvent was removed on a rotary evaporator. The colorless product (41.7 g, 96%, no impurities were observed in the NMR spectrum) was dissolved in refluxing hexane-benzene (9:1). Upon cooling, the product (34.95 g, 80%, mp 85-87°C) was obtained as colorless crystals. Additional product could be obtained from the mother liquor by repeated crystallization; however, combining and processing several batches is recommended. The NMR and IR spectra were identical with those of an authentic sample.

IR - Figure 14; NMR - Figure 15 (See Appendix)

Preparation of Bis[3-(1,1,3,3-tetramethyldisiloxanyl)phenyl] Carbonate and Bis[3-(3-vinyl-1,1,3-trimethyldisiloxanyl)phenyl] Carbonate Comonomer (J2332-05)

In a 500-ml three-neck flask were combined 1.39 g (0.015 mole) of methylvinylchlorosilane and 4.73 g (0.05 mole) of dimethylchlorosilane with one hundred ml of anhydrous ethyl ether, distilled from lithium aluminum hydride. To the reaction mixture was added 6.48 g (0.063 mole) of triethylamine, distilled from phenyl isocyanate. A pressure-equalizing funnel was used to add 11.5 g (0.032 mole) of bis[3-(hydroxydimethylsilyl)-phenyl] carbonate dissolved in 75 ml of dry ethyl ether over a period of fifteen minutes. The reaction mixture was stirred for about two hours. Two hundred ml of petroleum ether was used to dilute the mixture. The salts were filtered off with a medium porosity fritted-glass funnel and washed with 200 ml of petroleum ether. The solvent was removed on a rotary evaporator. Vacuum distillation of the residue through a short path distillation column yielded 9.0 g (58%) of material boiling at 160-170°C at 30 microns. From the NMR spectrum the product contained 14 percent vinyl groups. A total of six runs was made with yields ranging from 57 to 82 percent. The vinyl content was varied by changing the amounts of bis[3-(3-vinyl-1,1,3-trimethyldisiloxanyl)phenyl] carbonate incorporated.

J2332-42A	10 percent vinyl present
J2332-05	15 percent vinyl present
J2332-18	25 percent vinyl present
J2332-39A, 58, 81	30 percent vinyl present

IR - Figure 16 (See Appendix)

Preparation of POLYSAC-10, -20, -30 Precursor by Silver Acetate Oxidation (J2332-09)

The procedure used was the same as that used for the silver acetate oxidation of bis[3-(dimethylsilyl)phenyl] carbonate, except that no crystals were formed or isolated. The amounts used were 9.0 g of the mixed

disiloxanyl carbonates in 111 ml of dry tetrahydrofuran, 12.5 ml of water and 7.44 g of silver acetate. The yield was 9.10 g of disilanol.

IR - Figure 17 (See Appendix)

Bis[3-(1,1,3,3-tetramethyldisiloxanyl)phenyl] Carbonate (J2725-41)

A 1000-ml, three-necked flask was equipped with mechanical stirring, nitrogen inlet, an addition funnel and a cooling bath. Triethylamine (21.4 g, 0.2118 mole) and n-hexane were added to the reaction flask and cooled in a Dry Ice-acetone bath (-78°C). Dimethylchlorosilane (20.07 g, 0.2188 mole) was added in a single portion. A solution of bis[3-(hydroxydimethylsilyl)phenyl] carbonate (34.45 g, 0.09645 mole) in anhydrous diethyl ether (200 ml) was placed in the addition funnel and added dropwise to the reaction mixture over a period of 30 minutes. After completion of the addition, the thick slurry was stirred for 15 minutes at -78°C and then at ambient temperature for one hour. With cooling, 150 ml of water was added dropwise with stirring (10 minutes). The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and the solvent was removed on a rotary evaporator. Distillation of the residual oil gave 40.4 g (89%) of the product [bp 158-160°C (0.005 mm)].

IR - Figure 18; NMR - Figure 19 (See Appendix)

Preparation of Bis[3-(3-vinyl-1,1,3-trimethyldisiloxanyl)phenyl] Carbonate (J2749-37)

The procedure used was the same as the preceding one. The quantities of materials were 8.82 g (0.083 mole) of methylvinylchlorosilane, 8.38 g (0.083 mole) of triethylamine, a total of 250 ml of dry ethyl ether, and 15.0 g (0.041 mole) of bis[3-(hydroxydimethylsilyl)phenyl] carbonate. Distillation at 190°C (0.005 mm) gave a yield of 16.9 g (81%) of product.

IR - Figure 20; NMR - Figure 21 (See Appendix)

Reaction of Bis[3-(1, 1, 3-trimethyl-3-vinyldisilanoxyl)phenyl] Carbonate with Palladium on Carbon and Water (J2725-37)

A. A solution of bis[3-(1, 1, 3-trimethyl-3-vinyldisilanoxyl)phenyl] carbonate (1.0 g, 0.002125 mole) in tetrahydrofuran (10 ml), 5% palladium on carbon (50 mg), and a buffered aqueous solution (2 ml, pH 7.0) were placed in a 25-ml round-bottomed flask and refluxed for one hour. Gas evolution was not observed. After cooling to room temperature, the reaction mixture was filtered and methylene chloride (100 ml) was added. The organic layer was washed thoroughly with water, dried over anhydrous sodium sulfate, filtered, and the solvent was removed in vacuo (bath temperature 35°C). The residual oil consisted of a mixture of bis[3-(3-hydroxy-1, 1, 3-trimethyl-3-vinyldisiloxanyl)-phenyl] carbonate (10%) and bis[3-(3-hydroxy-1, 1, 3-trimethyl-disiloxanyl)phenyl] carbonate (90%).

B. The above experiment was repeated with the exception that isoprene (2 ml) was added to the tetrahydrofuran solution in order to scavenge hydrogen. NMR analysis indicated that the reaction mixture consisted of bis[3-(3-hydroxy-1, 1, 3-trimethyl-3-vinyldisiloxanyl)phenyl] carbonate (60%) and bis[3-(3-ethyl-3-hydroxy-1, 1, 3-trimethyldisiloxanyl)phenyl] carbonate (40%).

C. Similarly, the addition of 1,4-cyclooctadiene (3 ml) gave bis[3-(3-hydroxy-1, 1, 3-trimethyl-3-vinyldisiloxanyl)phenyl] carbonate (80%) and bis[3-(3-ethyl-3-hydroxy-1, 1, 3-trimethyldisiloxanyl)phenyl] carbonate (20%).

Bis[3-(3-hydroxy-1, 1, 3-trimethyl-3-vinyldisiloxanyl)phenyl] Carbonate (J2725-38)

A solution of bis[3-(1, 1, 3-trimethyl-3-vinyldisiloxanyl)phenyl)] carbonate (3.0 g, 0.0064 mole) in tetrahydrofuran (40 ml) and water (4.5 ml) were placed in a 100-ml, three-necked flask equipped with magnetic stirring, thermometer and a cooling bath. Silver acetate (2.49 g, 0.0152 mole) was added in portions over three hours while maintaining the internal

temperature at 0-5°C. The cooling bath was removed and the reaction mixture was stirred at ambient temperature overnight (15 hours). Methylene chloride (250 ml) was added and the organic layer was washed with a buffered aqueous solution (pH 7.0; 2 x 100 ml), dried over anhydrous sodium sulfate and filtered. Evaporation of the solvent (bath temperature 34°C) gave the product as a colorless oil in quantitative yield.

IR - Figure 22; NMR - Figure 23 (See Appendix)

Bis[3-(3-hydroxy-1,1,3,3-tetramethyldisiloxanyl)phenyl] Carbonate (J2725-39)

A 500-ml flask was equipped with a magnetic stirring bar and a reflux condenser. 5% Palladium on carbon (0.25 g) was placed in the flask, followed by a solution of bis[3-(1,1,3,3-tetramethyldisilanoxyl)phenyl] carbonate (11.1 g, 0.02318 mole) in tetrahydrofuran (120 ml) and a buffered aqueous solution (30 ml, pH 7.0). The reaction mixture was refluxed until gas evolution was completed (45 minutes). The reaction mixture was cooled to ambient temperature and filtered. Methylene chloride (250 ml) was added and the organic layer was washed with water (4 x 200 ml), dried over anhydrous sodium sulfate, filtered and the solvent was removed in vacuo. The bath temperature did not exceed 35°C. Careful evaporation of the solvent gave bis[3-(3-hydroxy-1,1,3,3-tetramethyldisiloxanyl)phenyl] carbonate in quantitative yield which was used directly in the subsequent polymerization experiments.

IR - Figure 24; NMR - Figure 25 (See Appendix)

Condensation of Mixture of Bis[3-(3-hydroxy-1,1,3,3-tetramethyl-disiloxanyl)phenyl] Carbonate, 3-(3-hydroxy-3-vinyl-1,1,3-trimethyl-siloxanyl)phenyl 3-(3-hydroxy-1,1,3,3-tetramethylsiloxanyl)phenyl Carbonate and Bis[3-(3-hydroxy-3-vinyl-1,1,3-trimethylsiloxanyl)phenyl] Carbonate (IV) (J2332-44)

In a small flask, equipped with a stirring bar, was combined 8.1357g of IV (determined to contain 30 percent vinyl groups) with 0.1153g of 2,4,6-trimethylpyridinium trifluoroacetate with hexane as solvent. Heat

was applied gradually with an oil bath until the temperature of the oil was 105°C. Total time of heating was 27 hours, 24 hours at 105°C. The polymerization was run under argon. The chain-extended material was honey colored and had a spreadable consistency. The polymer was dissolved with hexane and the catalyst was washed out with water. Methylene chloride was added to control emulsion formation. The solution was filtered and concentrated on a rotary evaporator. The molecular weight of this product was 11,000 as determined by vapor phase osmometry.

IR - Figure 26; NMR - Figure 27 (See Appendix)

Condensation of Bis[3-(3-hydroxy-1,1,3,3-tetramethyldisiloxanyl) phenyl] Carbonate (I) and Bis[3-(3-hydroxy-3-vinyl-1,1,3-trimethyl-disiloxanyl)phenyl] Carbonate (II) (J2749-48)

In a dry 250-ml three-neck round-bottom flask was placed under argon atmosphere 7.0 g (0.0137 mole) of I and 0.40 g (0.0007 mole) of II. Seventy-five ml of pyridine (distilled from calcium hydride) was added to the flask. A mechanical stirrer and paddle was used to stir the solution vigorously. An ice-water bath was used to cool the flask. A small amount of phosgene was added through a gas inlet tube just above the reaction mixture. As soon as a solid was formed the phosgene addition was stopped and the reaction was stirred vigorously. Intermittently more phosgene was added with intervals of stirring. The reaction was monitored by NMR by following the existence of peaks at 0.42 ppm(s), 0.53 ppm(s) and 0.70 ppm (unresolved doublet) with TMS externally set at 0.0 ppm. The 0.53 ppm decreased with time until the peak disappeared, which was noted after 23 hours of reaction time. The reaction mixture was worked up by diluting with methylene chloride to 200 ml and filtering off the salts. The salts were washed with methylene chloride. The filtrate was concentrated to a small volume by a rotary evaporator and the polymer was precipitated with anhydrous methanol.

The isolated polymer was white. The polymer was precipitated three more times from methylene chloride with methanol and dried. The weight of polymer isolated was 1.5 g (20%); inherent viscosity 0.29 dl/g (CH_2Cl_2, 25°C). Another run gave a yield of 4.4 g (59%), inherent viscosity 0.39 dl/g (CH_2Cl_2, 25°C).

NMR - Figures 28, 29, 30, 31, 32, 33 (See Appendix)

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APPENDIX

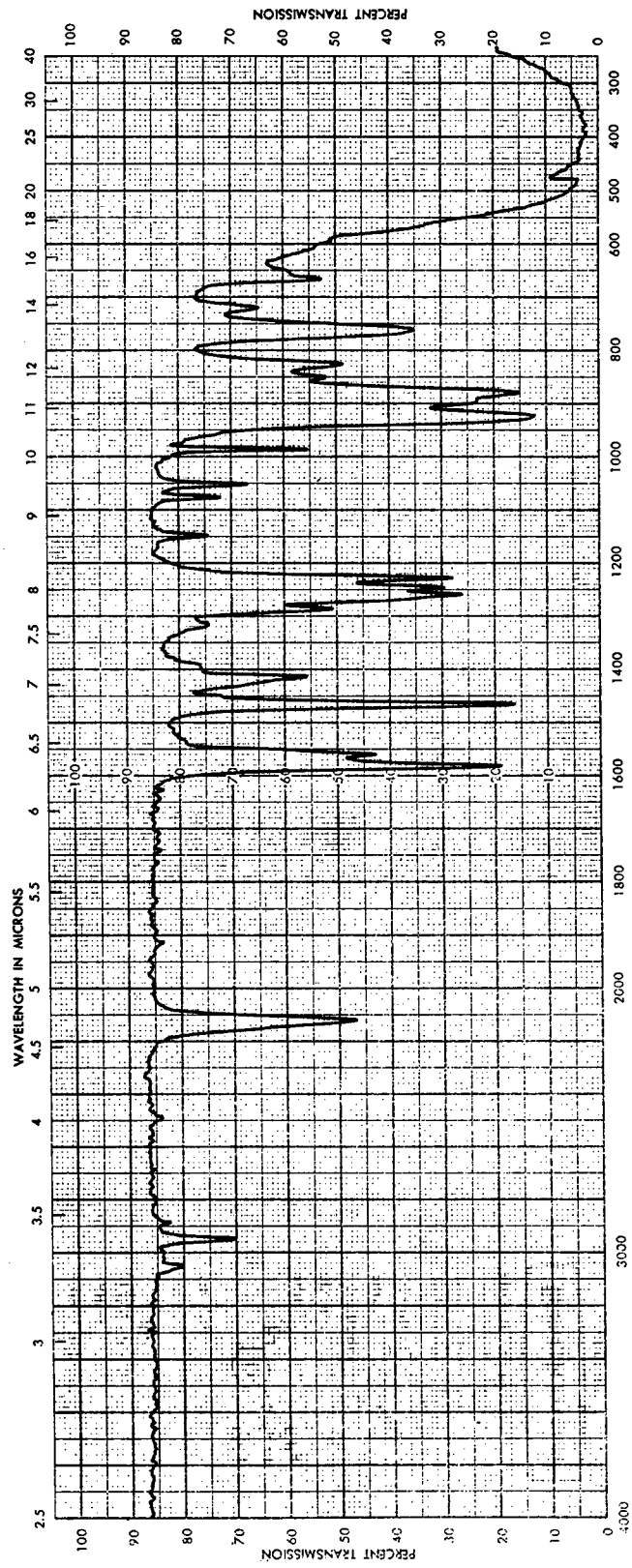

Figure 6. Infrared spectrum of 3-bromo phenoxydimethylsilane

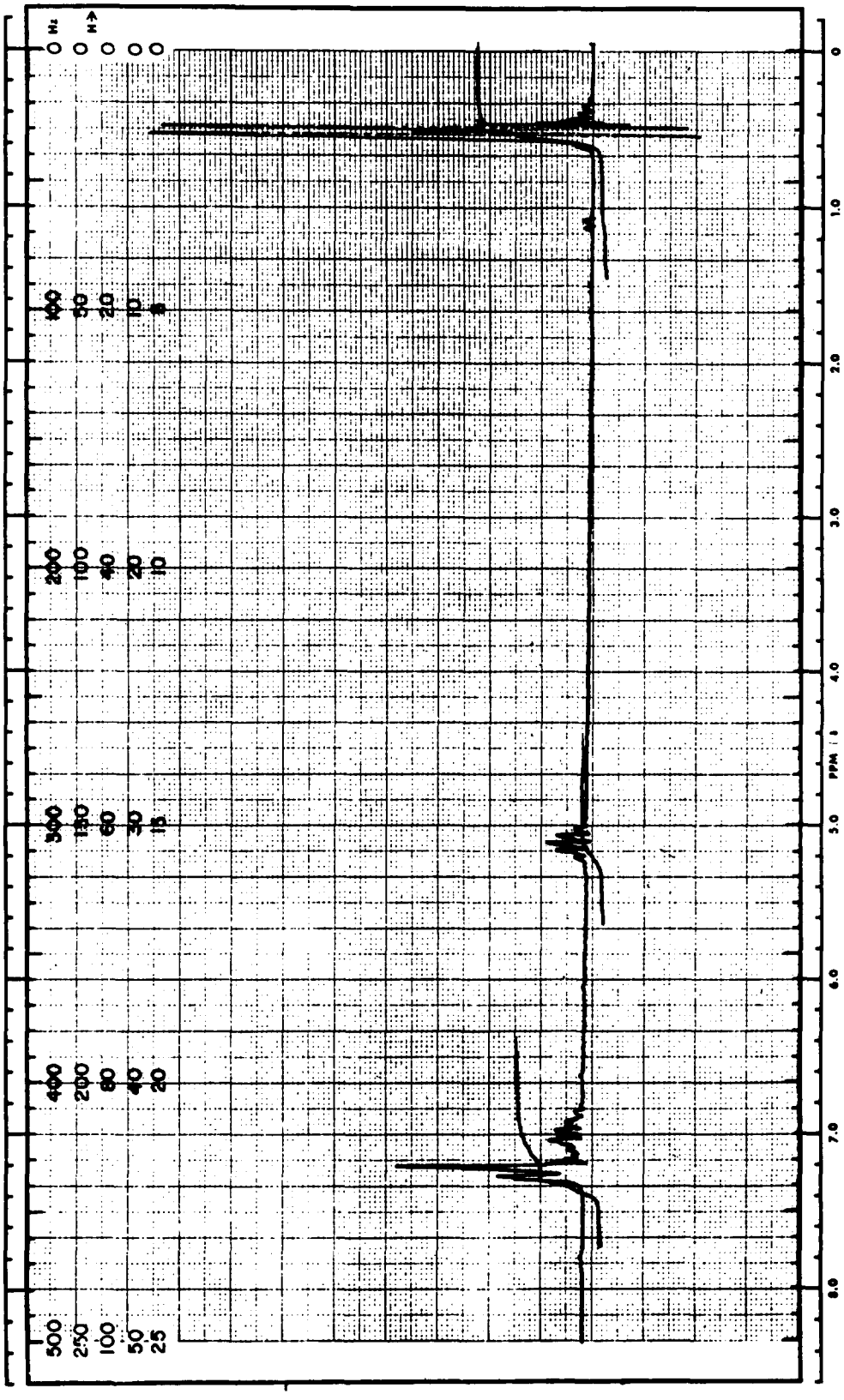

Figure 7. H-NMR spectrum of 3-bromophenoxydimethylsilane.

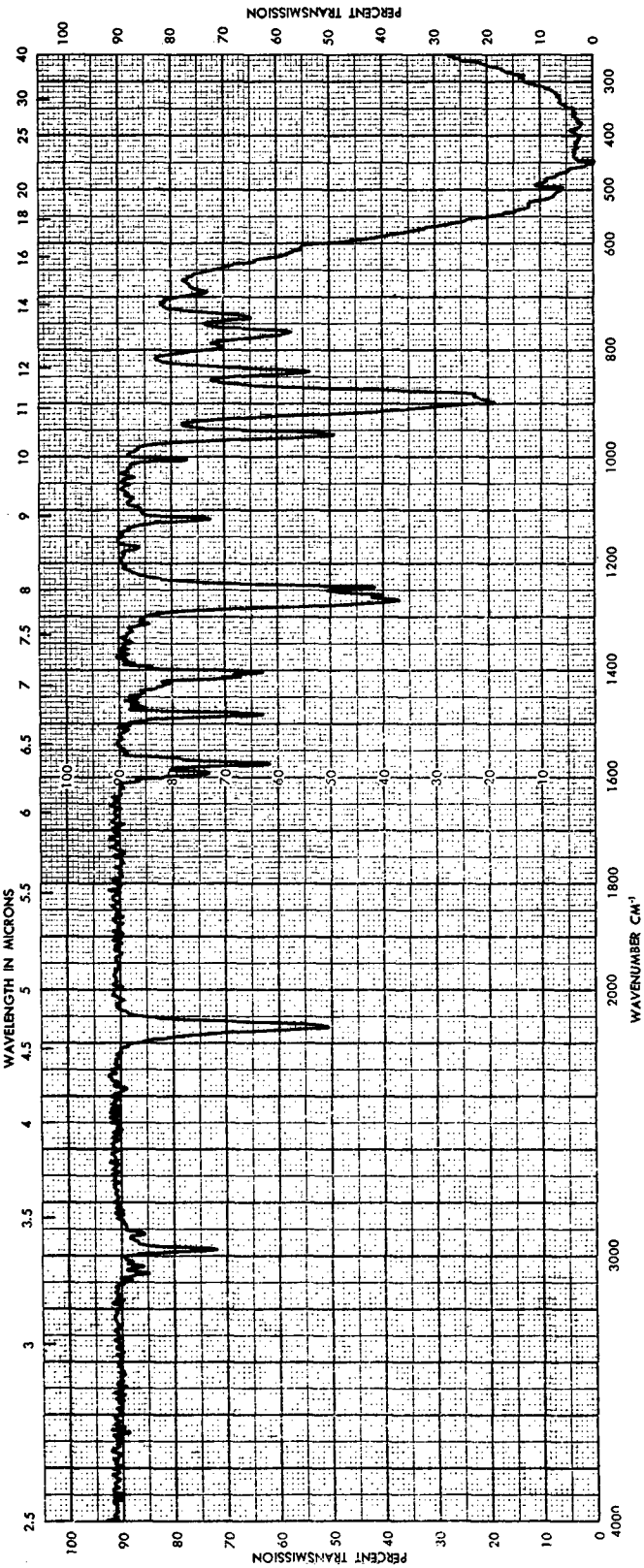

Figure 8. Infrared spectrum of 3-dimethylsilylphenoxydimethylsilane.

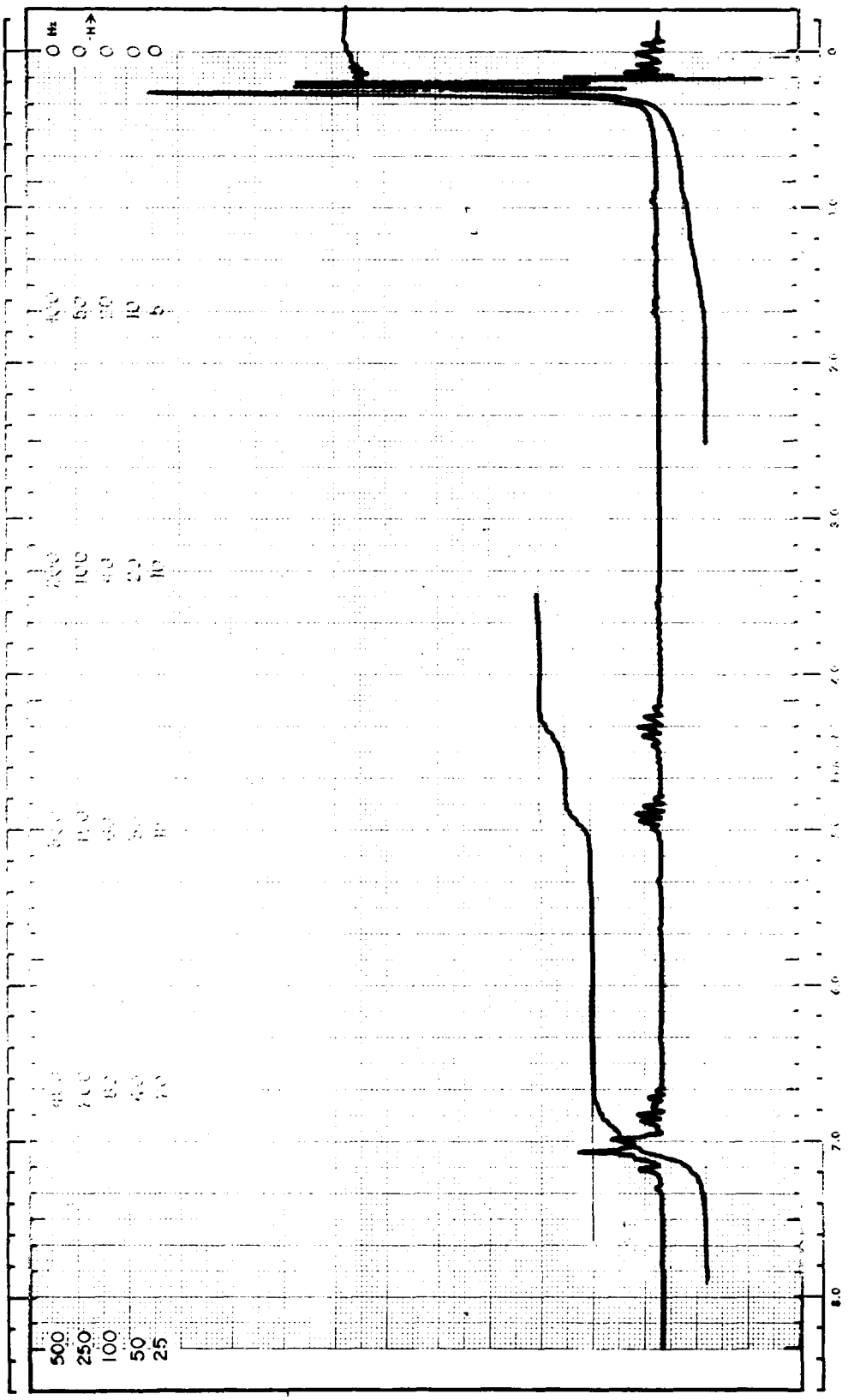

Figure 9. H-NMR spectrum of 3-(dimethyl silyloxy)phenyldimethylsilane.

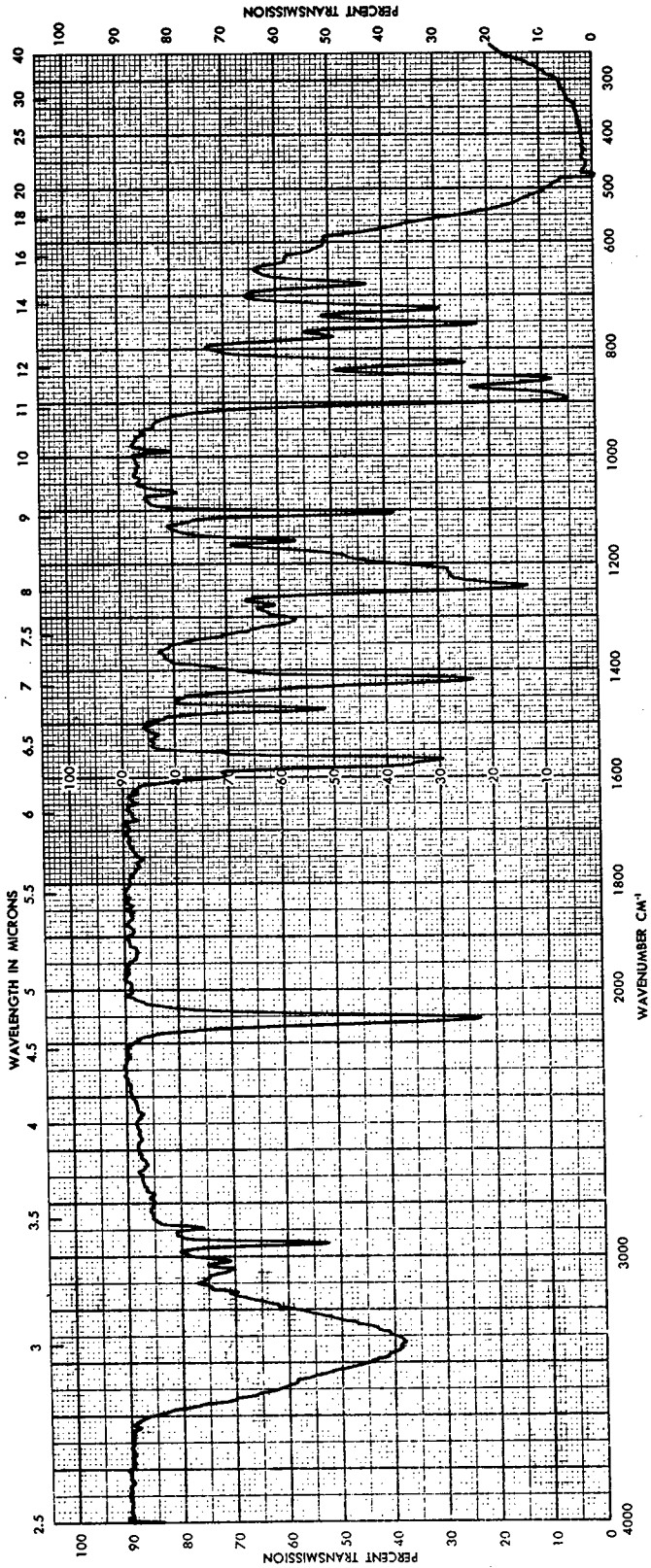

Figure 10. Infrared spectrum of 3-dimethyl silylphenol.

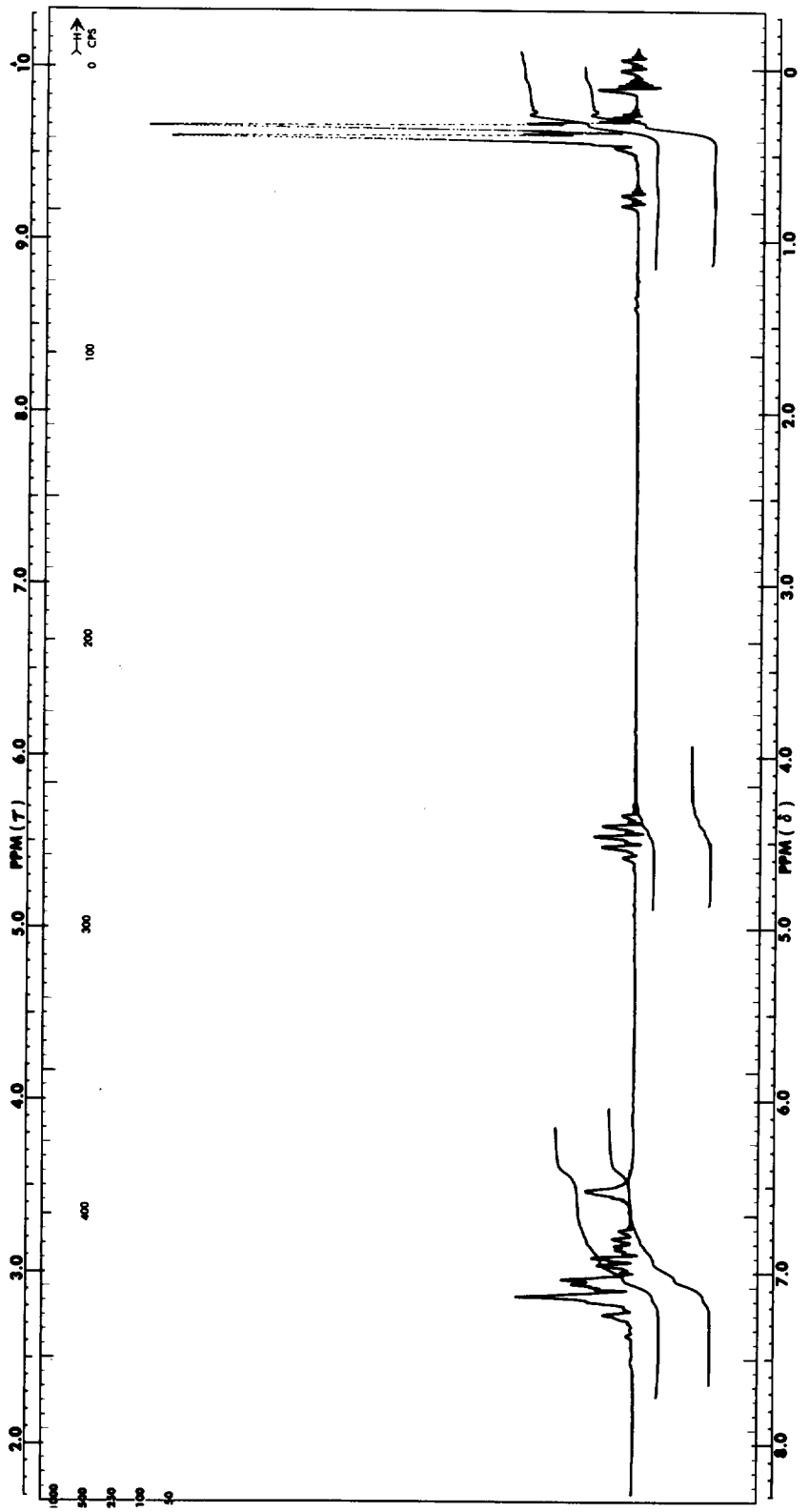

Figure 11. H-NMR spectrum of 3-dimethyl silylphenol.

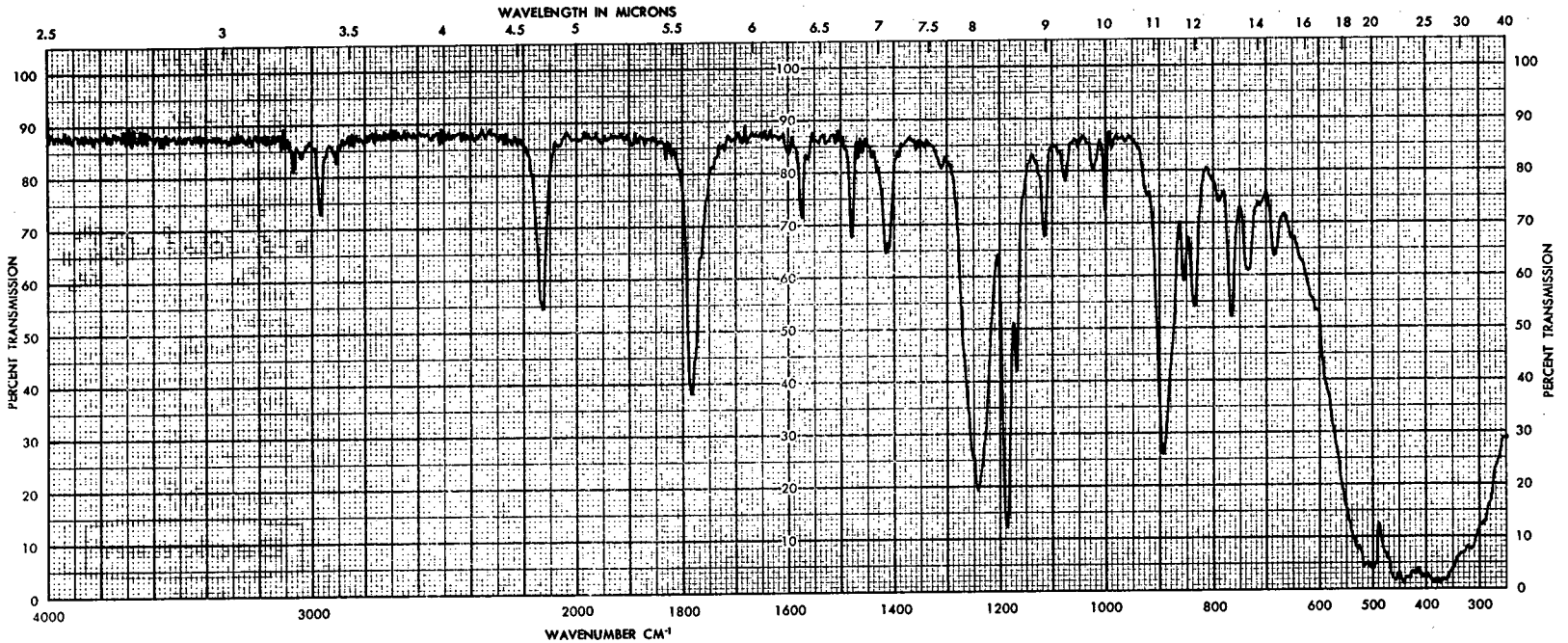

Figure 12. Infrared spectrum of bis[3-(dimethylsily)phenyl] carbonate.

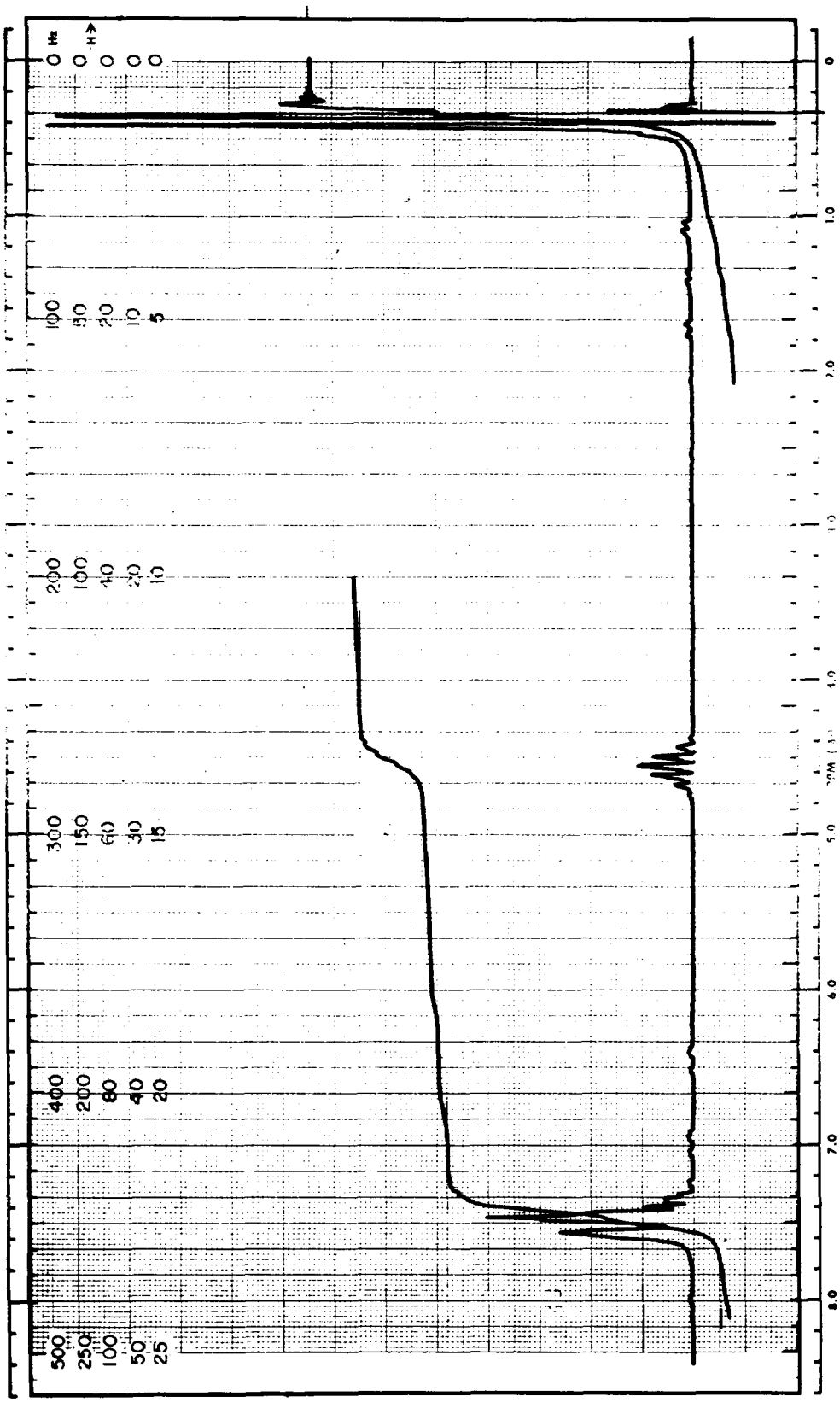

Figure 13. H-NMR spectrum of bis[3-(dimethylsilyl)phenyl]carbonate.

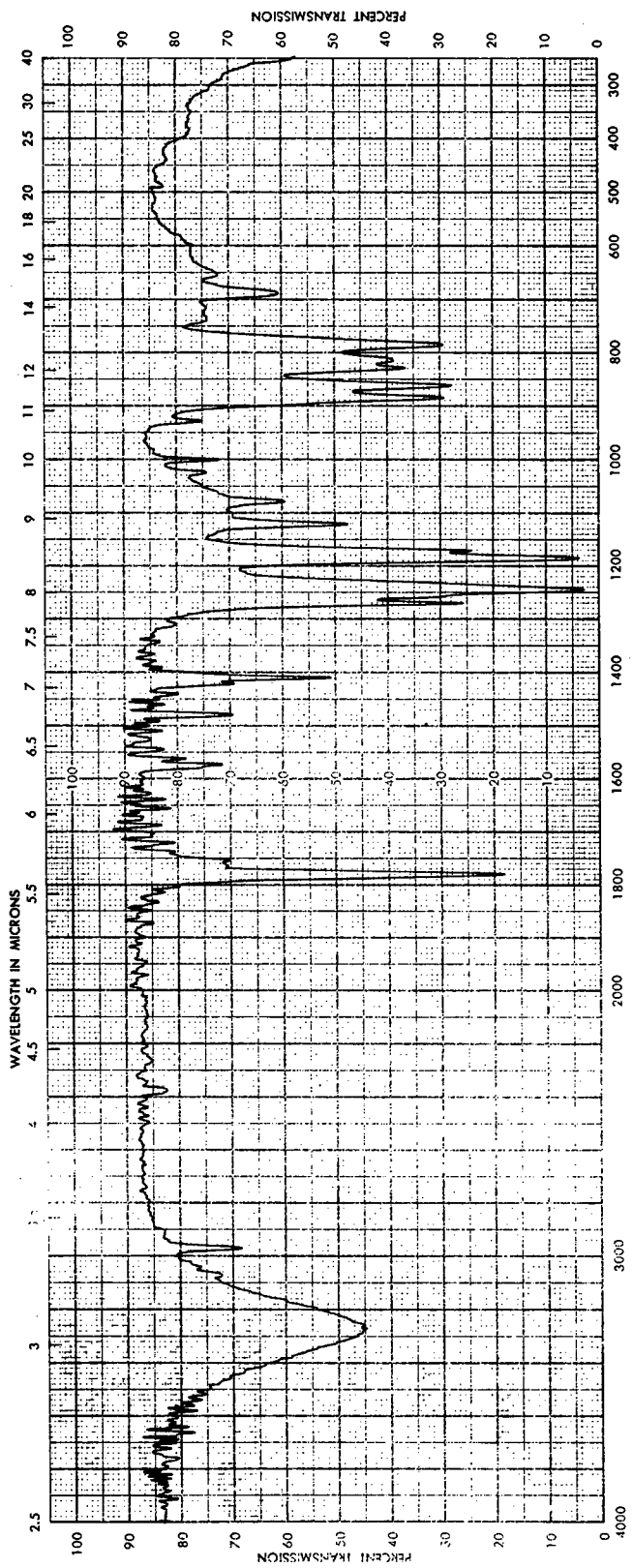

Figure 14. Infrared spectrum of bis [3-(hydroxydimethylsilyl)phenyl] carbonate (KBr pellet).

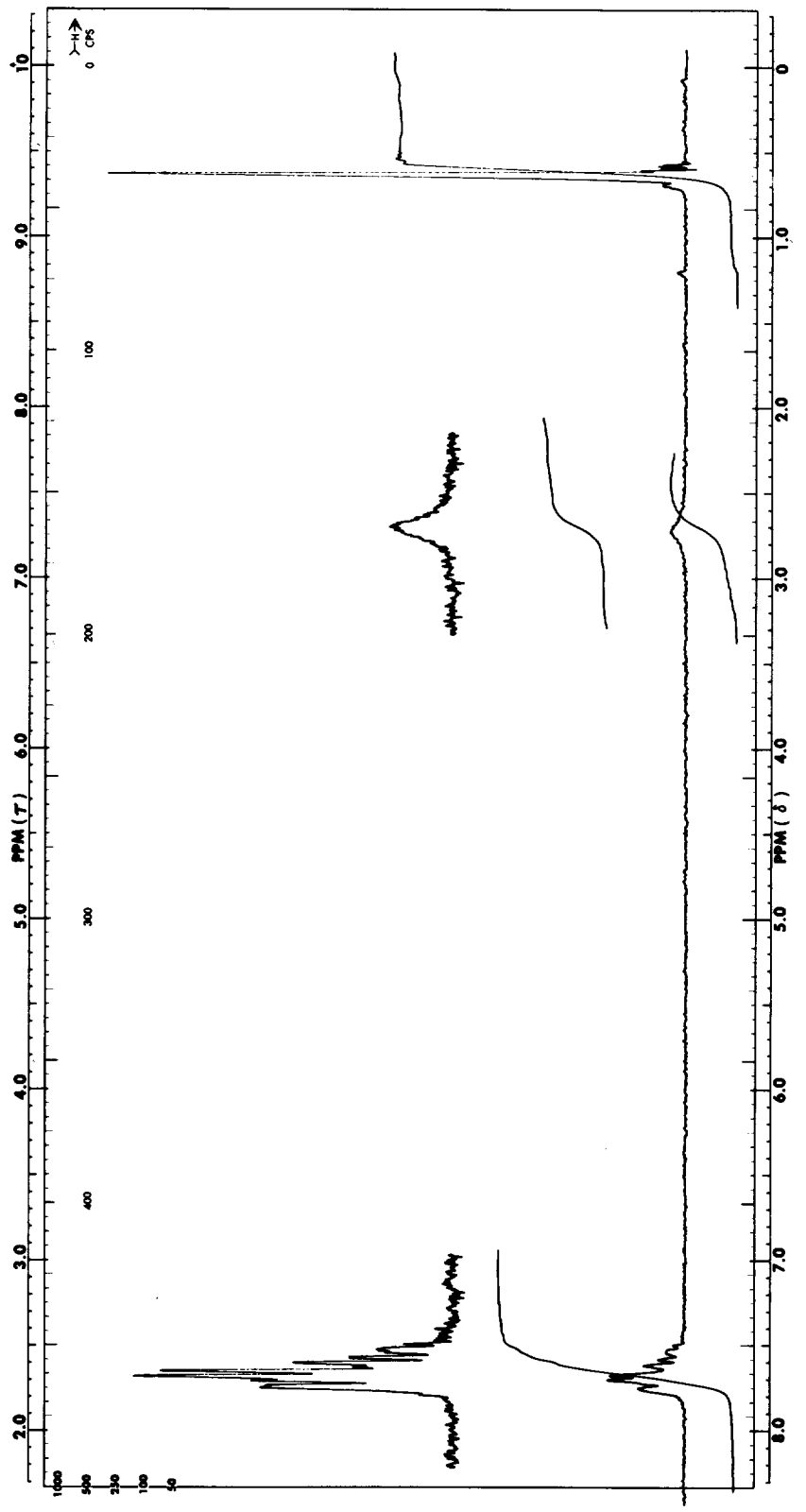

Figure 15. H-NMR spectrum of bis [3-(hydroxydimethylsilyl)phenyl] carbonate.

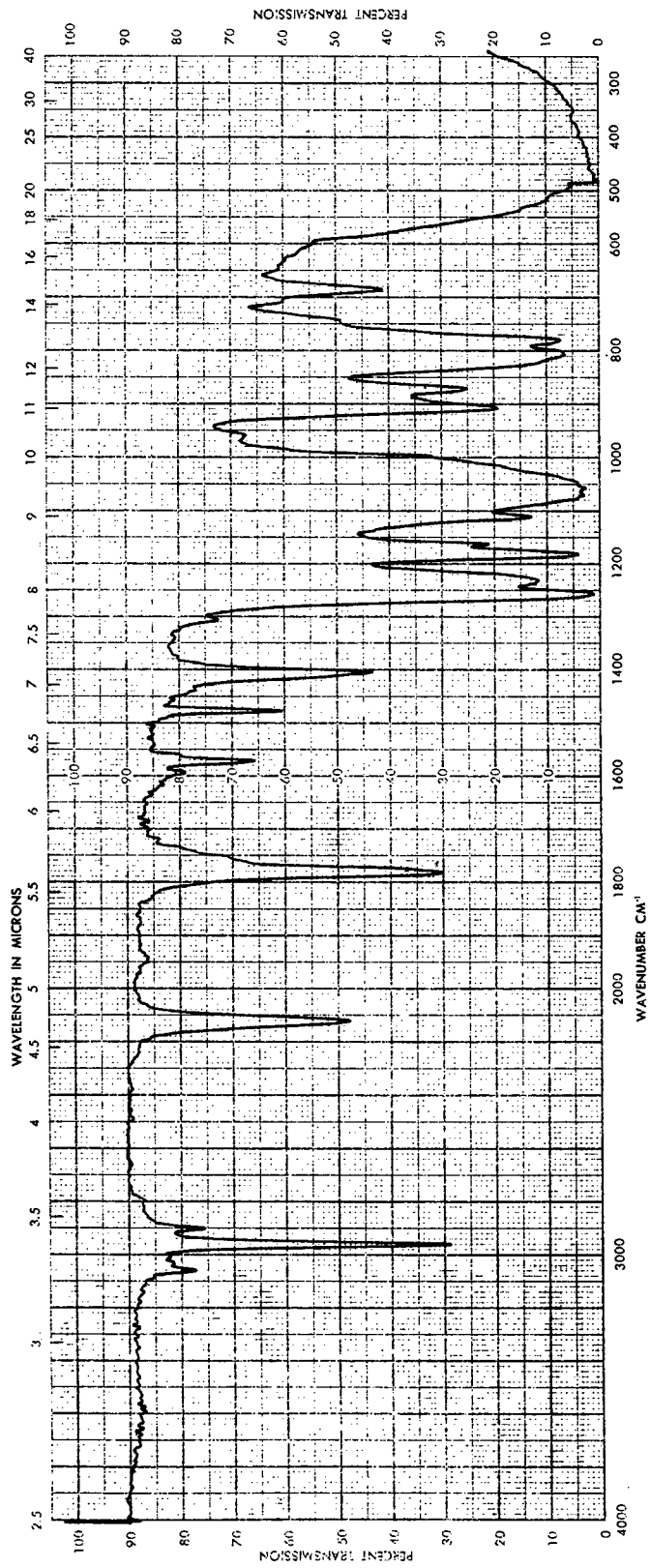

Figure 16. Infrared spectrum of bis [3-(1,1,3,3-tetramethyldisiloxanyl)phenyl] carbonate and bis:[3-(1,1,3-trimethyl-3-vinyldisiloxanyl)phenyl] carbonate comonomer.

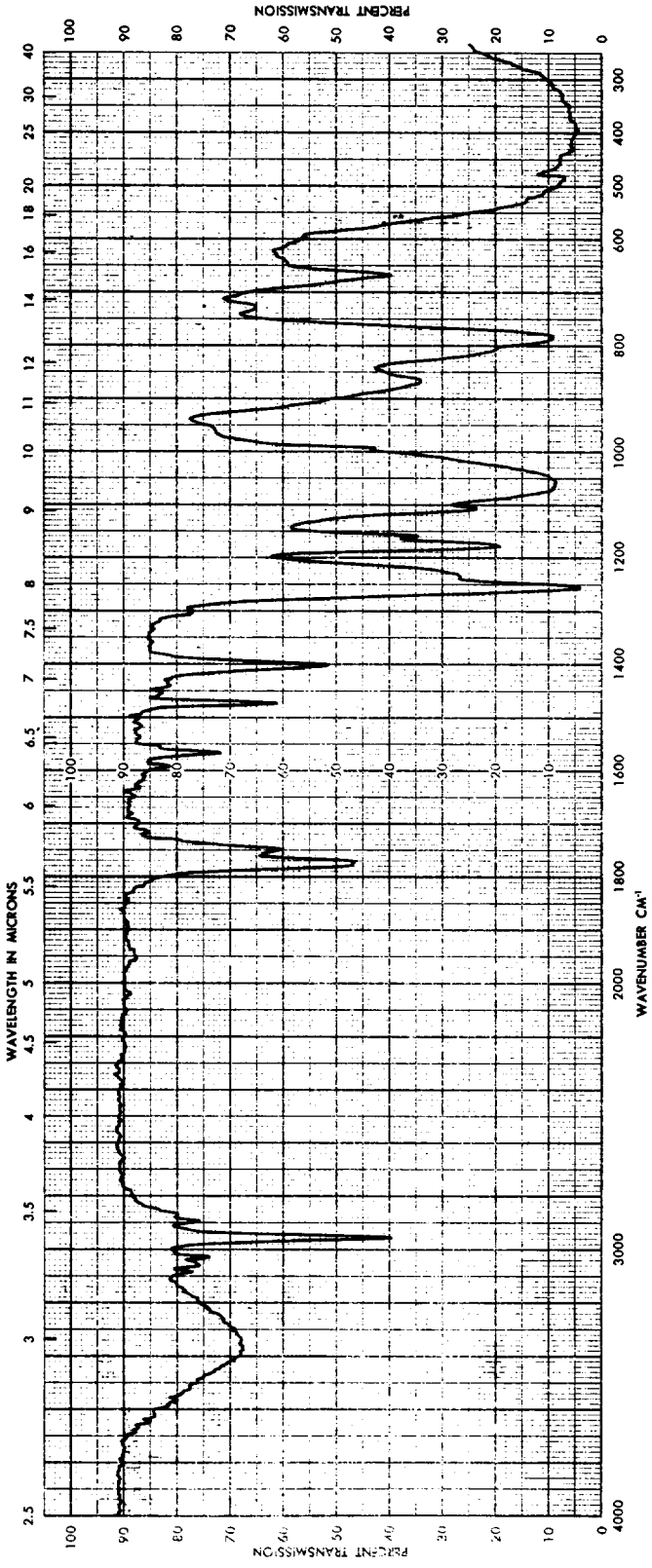

Figure 17. Infrared spectrum of POLYSAC-30 precursor.

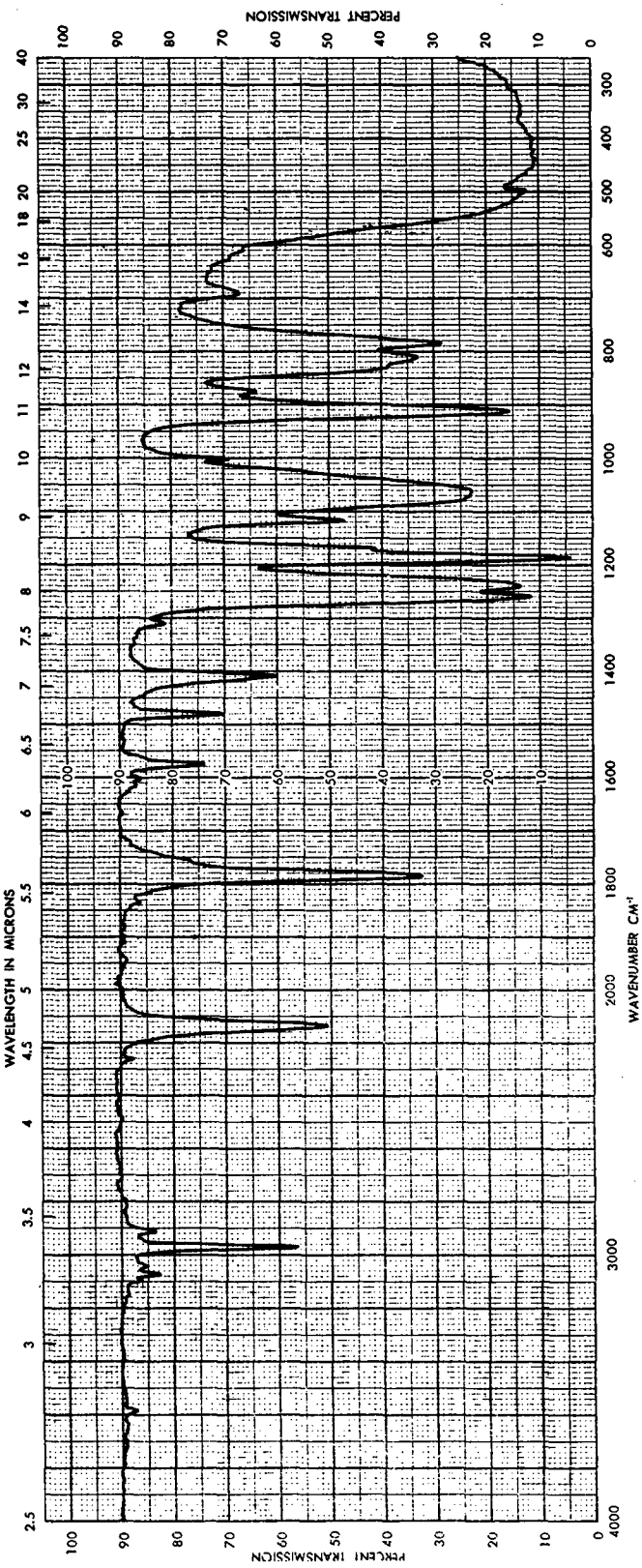

Figure 18. Infrared spectrum of bis[3-(1,1,3,3-tetramethyldisiloxanylphenyl)] carbonate.

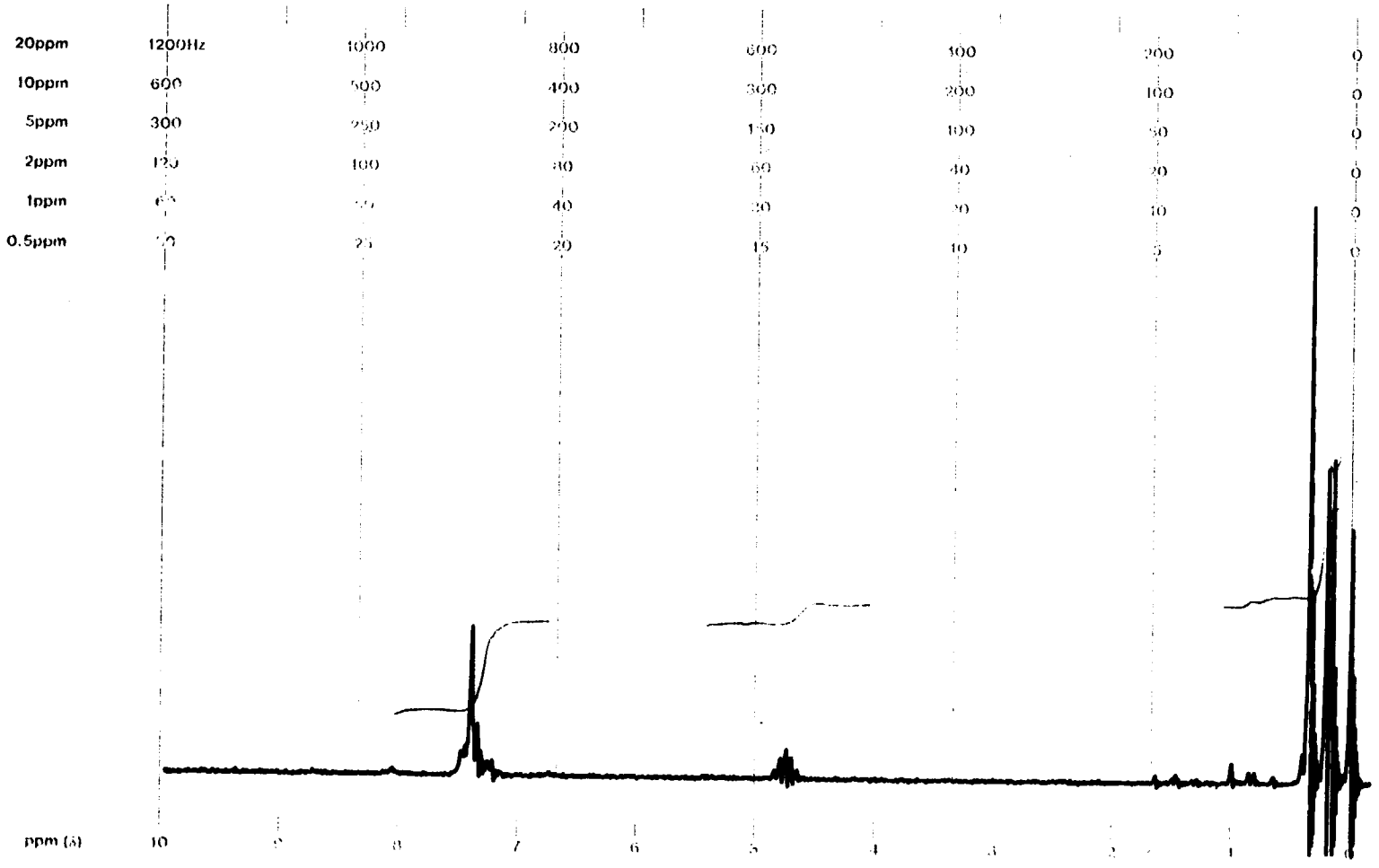

Figure 19. H-NMR spectrum of bis[3-(1,1,3,3-tetramethyldisiloxanyl)phenyl] carbonate.

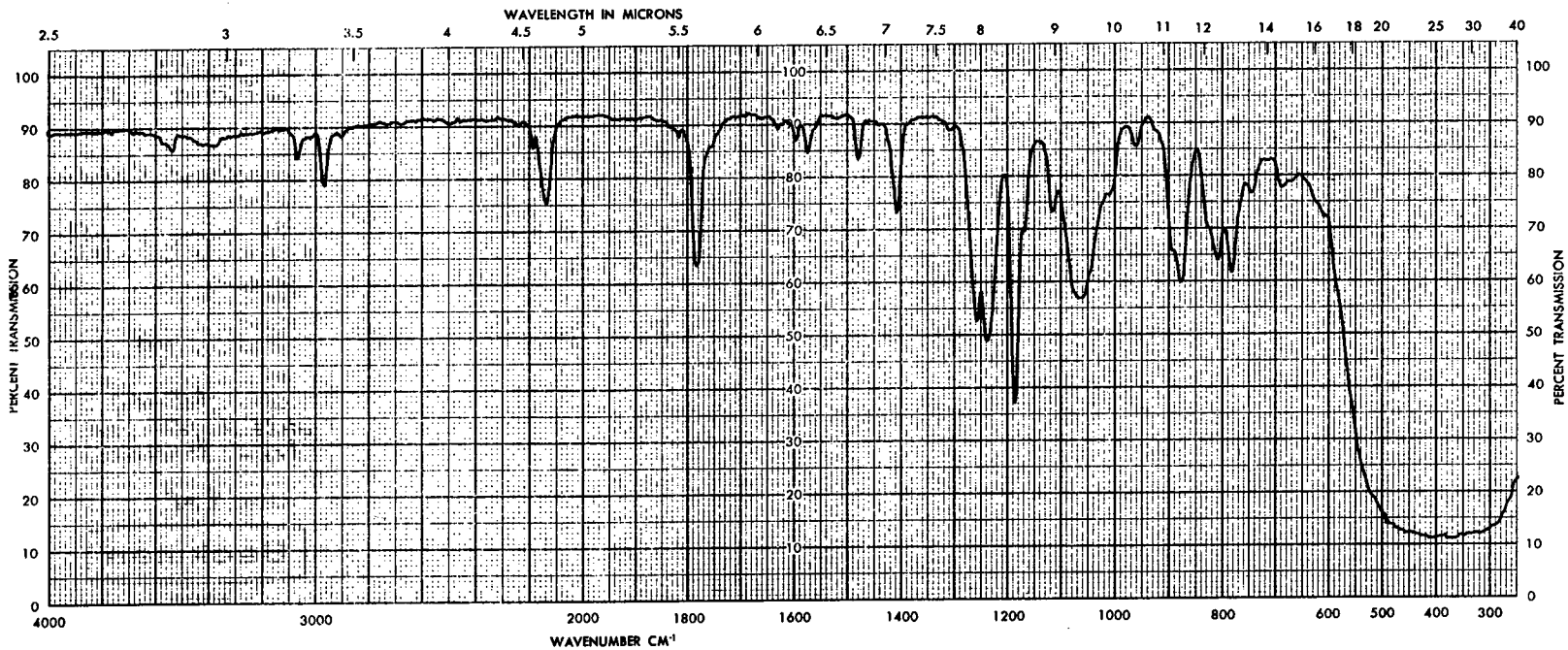

Figure 20. Infrared spectrum of bis [3-(1,1,3-trimethyl-3-vinyldisiloxanyl)phenyl] carbonate.

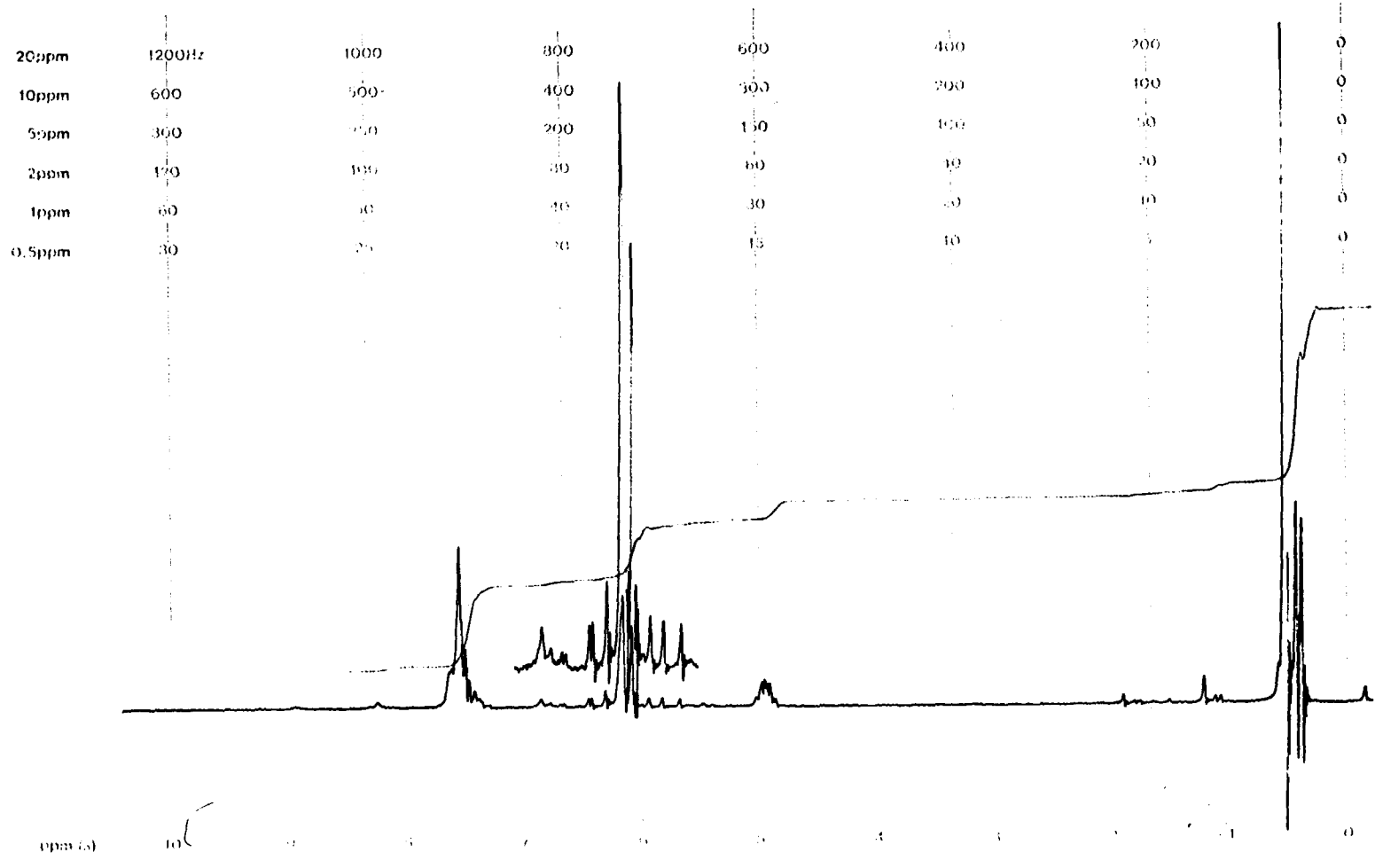

Figure 21. H-NMR spectrum of bis [3-(1,1,3-trimethyl-3-vinyldisiloxanyl)phenyl] carbonate.

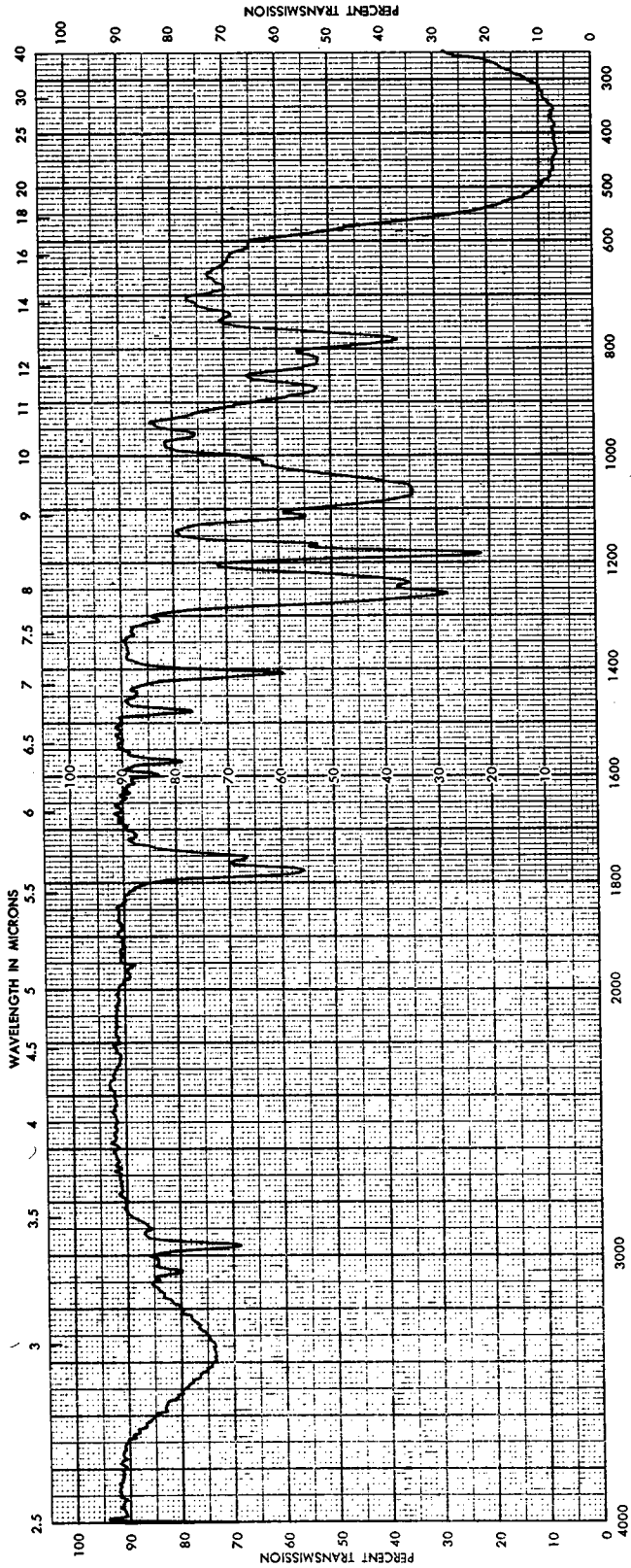

Figure 22. Infrared spectrum of bis [3-(3-hydroxy-1,1,3-trimethyl-3-vinyldisiloxanyl)phenyl] carbonate.

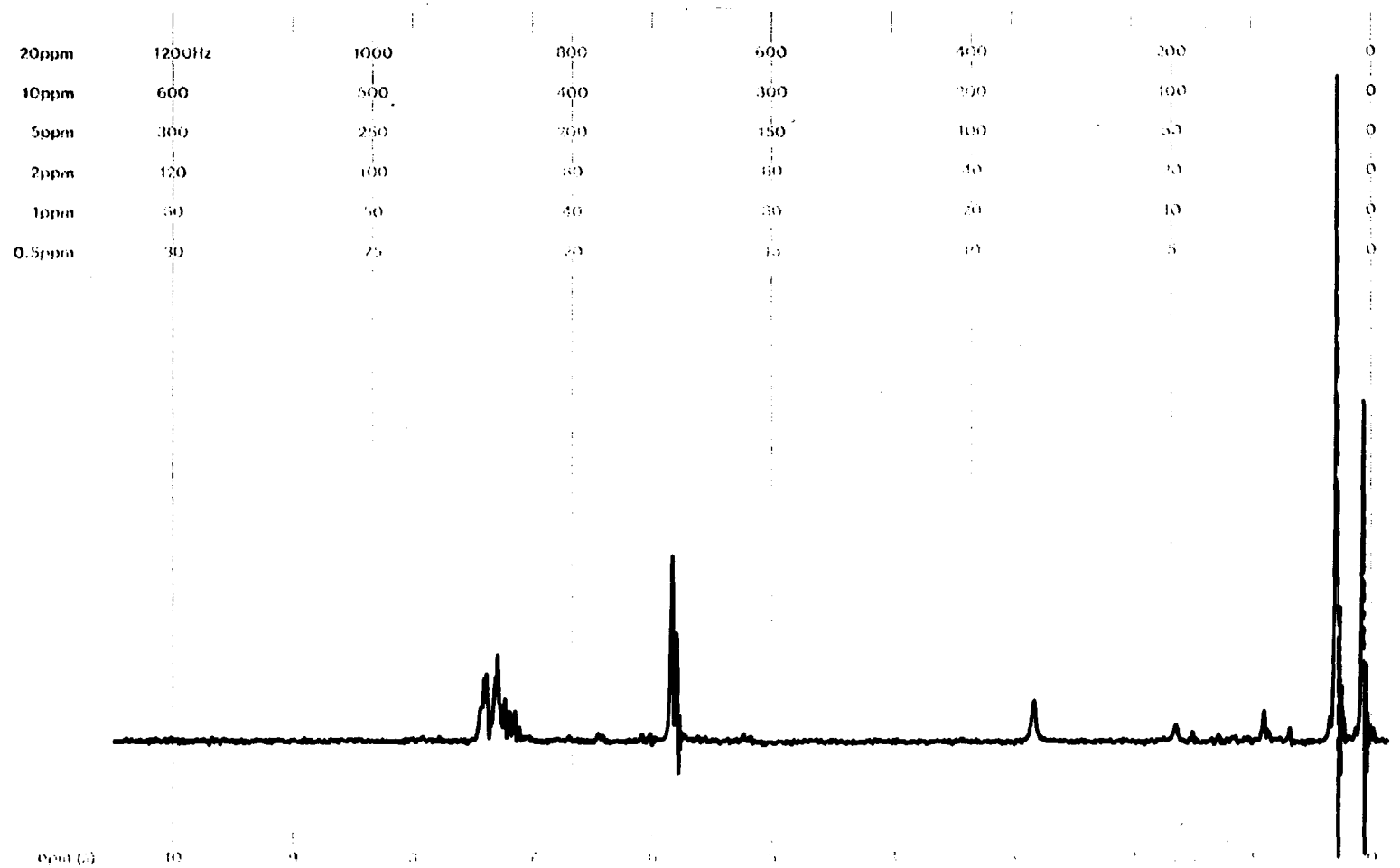

Figure 23. H-NMR spectrum of bis[3-(3-hydroxy-1,1,3-trimethyl-3-vinyldisiloxany)phenyl] carbonate.

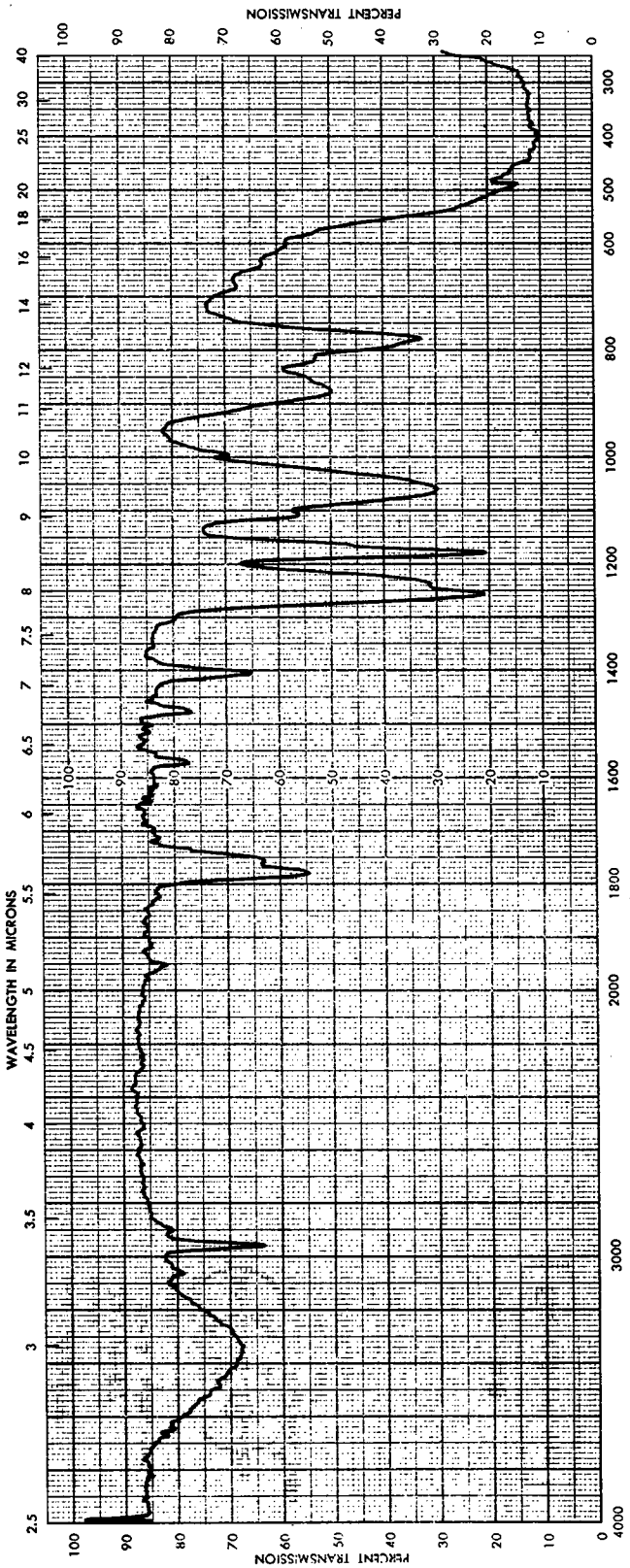

Figure 24. Infrared spectrum of bis[3-(3-hydroxy-1,1,3,3-tetramethyldisiloxanyl)phenyl] carbonate.

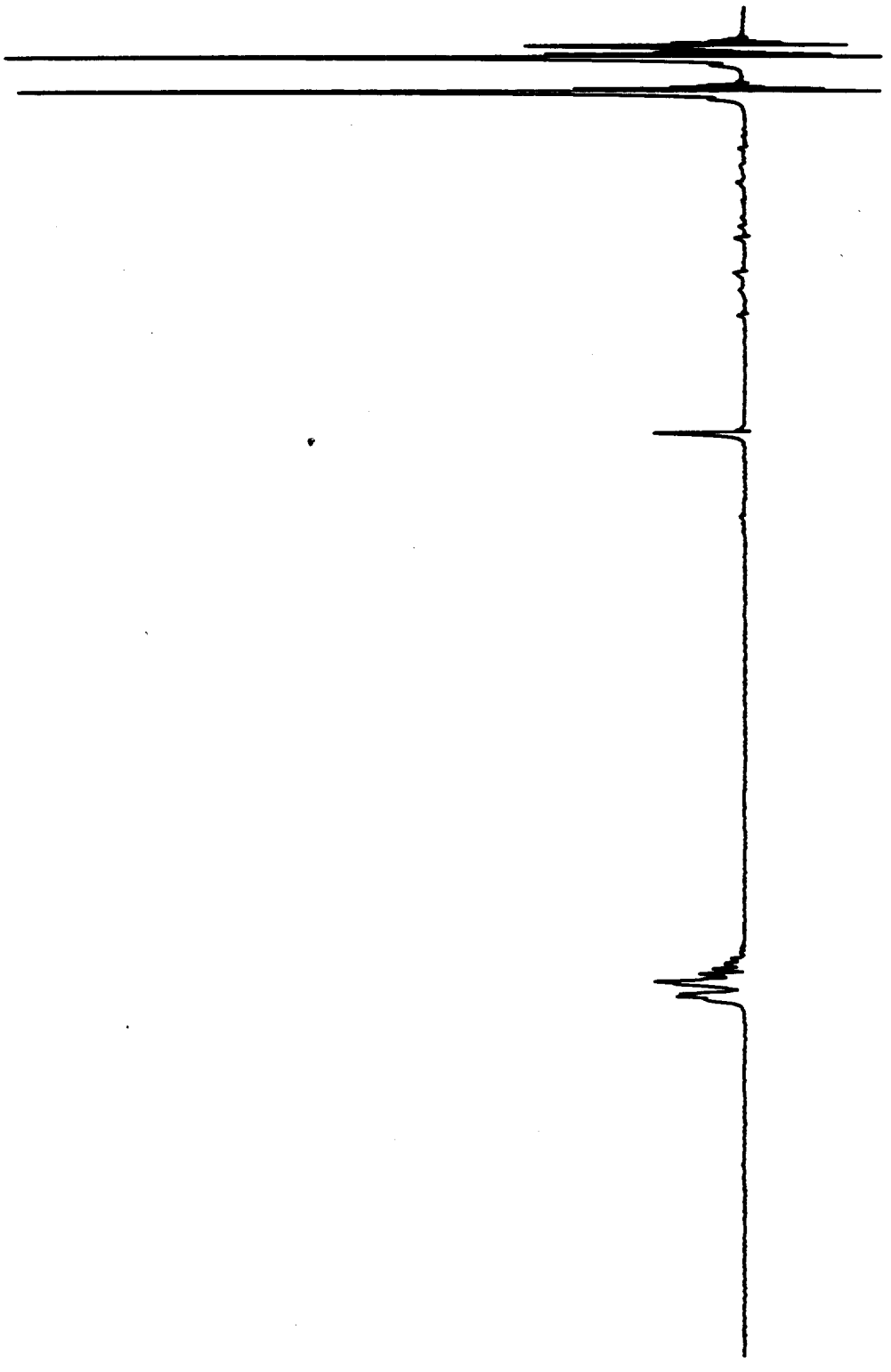

Figure 25. H-NMR spectrum of bis[3-(3-hydroxy-1,1,3,3-tetramethyldisiloxanyl)phenyl] carbonate.

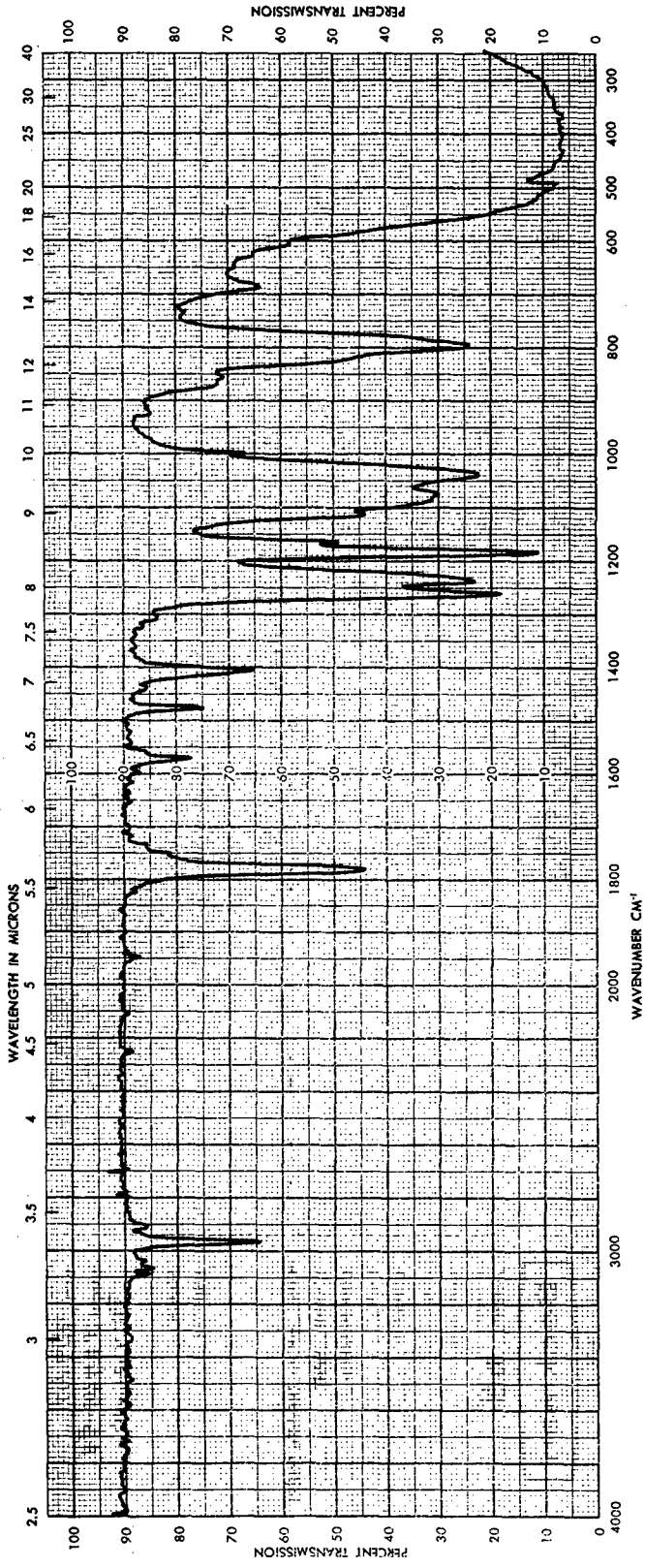

Figure 26. Infrared spectrum of POLYSAC-10 from HRTTT process.

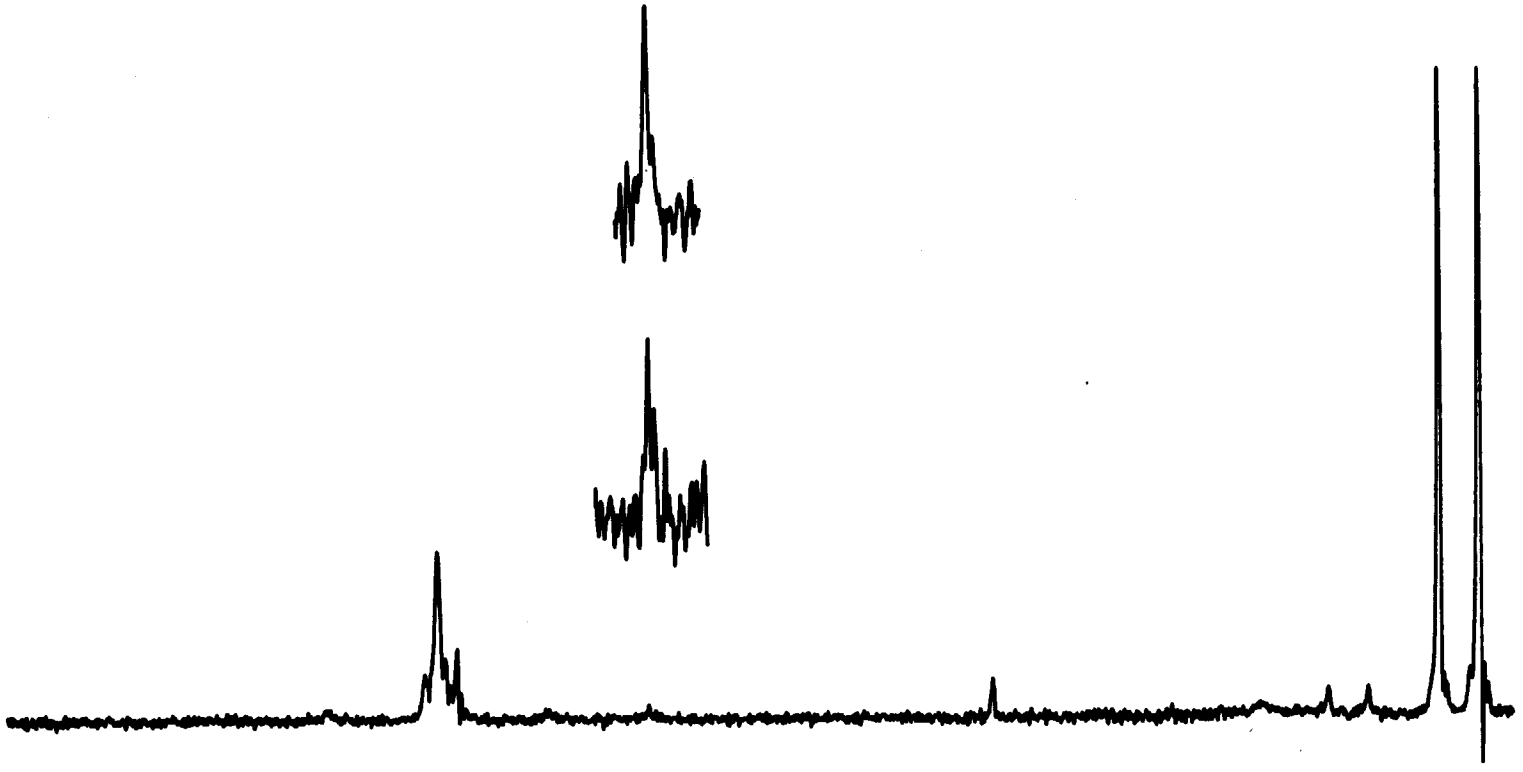

Figure 27. H-NMR spectrum of POLYSAC-10 from HRTTT process.

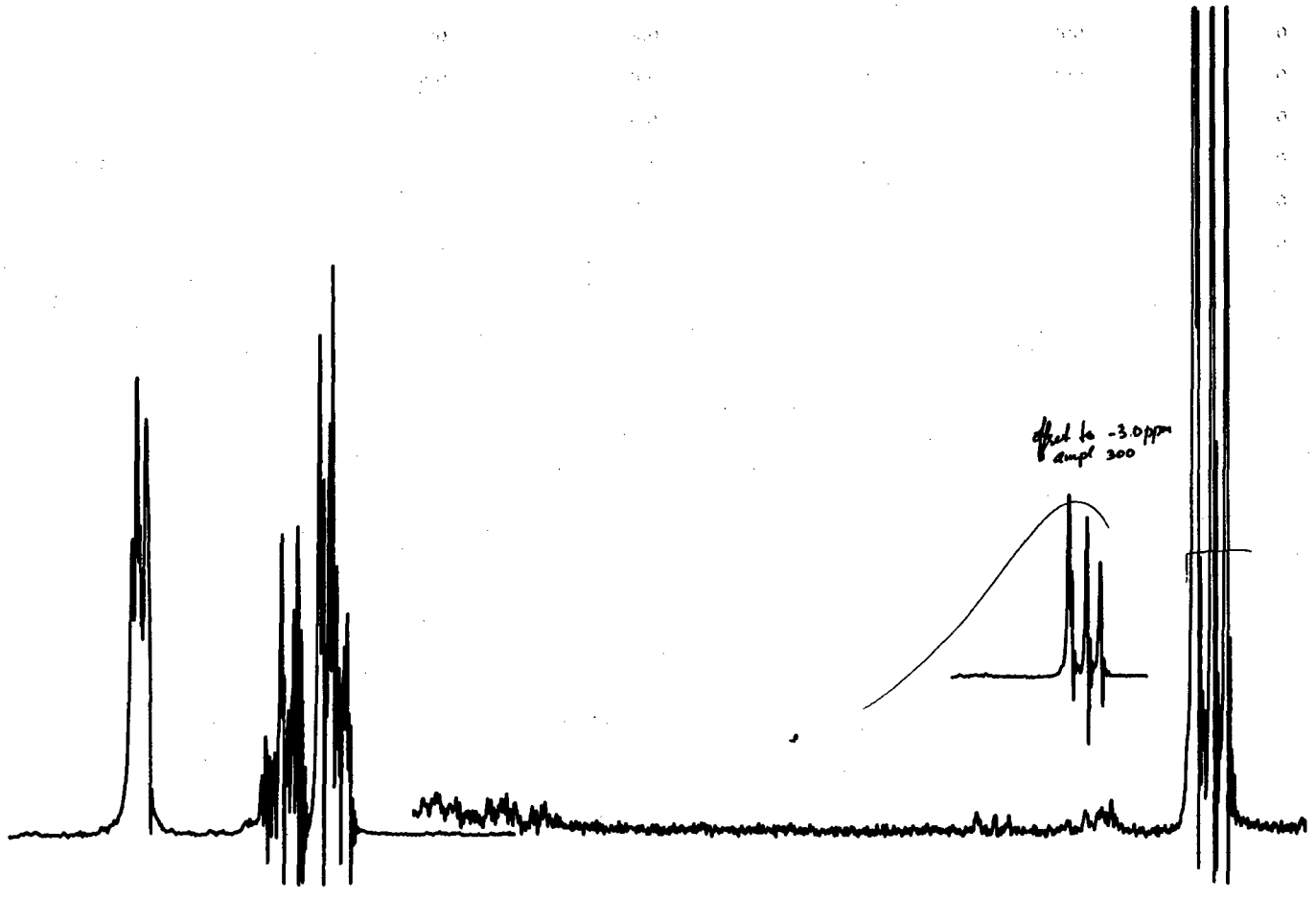

Figure 28. H-NMR spectrum of polymerization of POLYSAC-5 by HRTTT process. Aliquot No. 1.

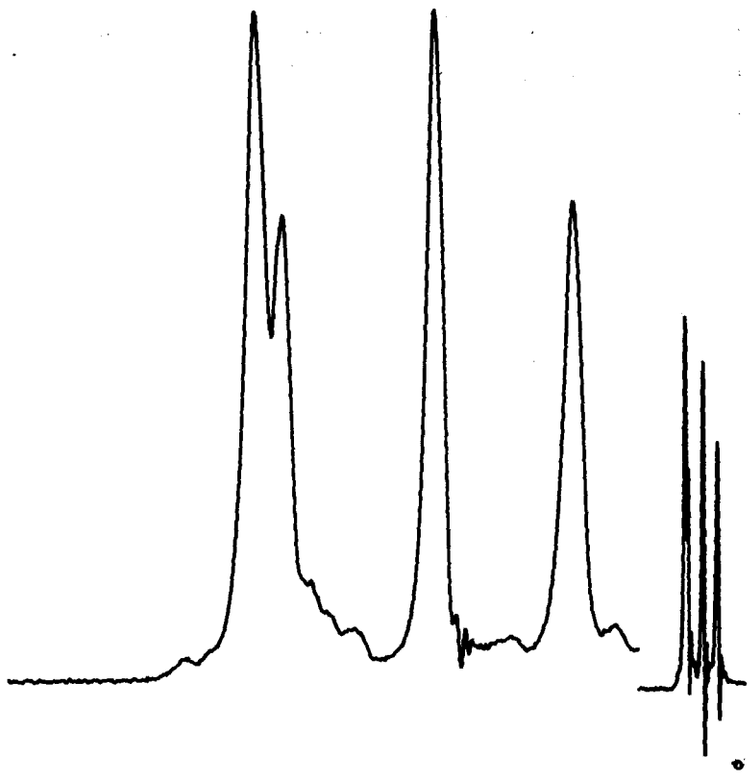

Figure 29. H-NMR spectrum of polymerization of POLYSAC-5 by HRTTT process. Aliquot No. 1 expanded.

Figure 30. H-NMR spectrum of polymerization of POLYSAC-5 by HRTTT process. Aliquot No. 2.

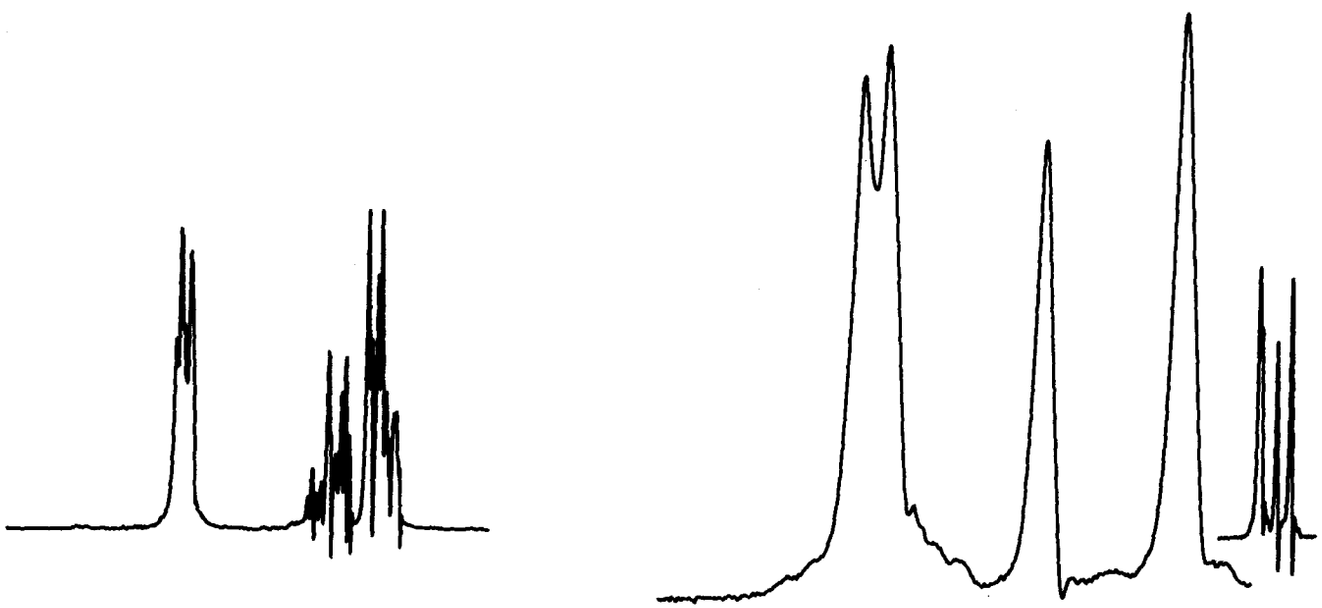

Figure 31. H-NMR spectrum of polymerization of POLYSAC-5 by HRTTT process. Aliquot No. 3.

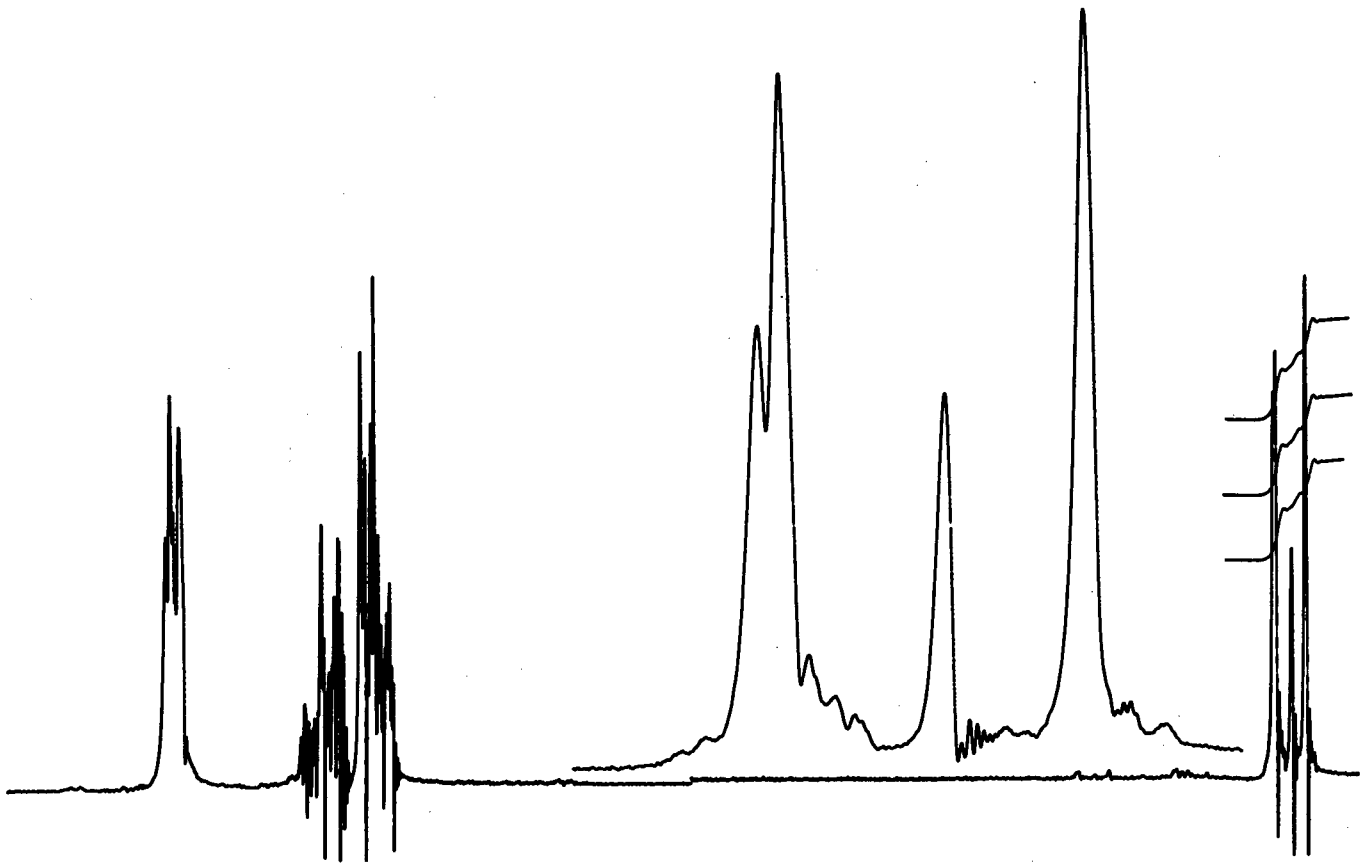

Figure 32. H-NMR spectrum of polymerization of POLYSAC-5 by HRTTT process. Aliquot No. 4.

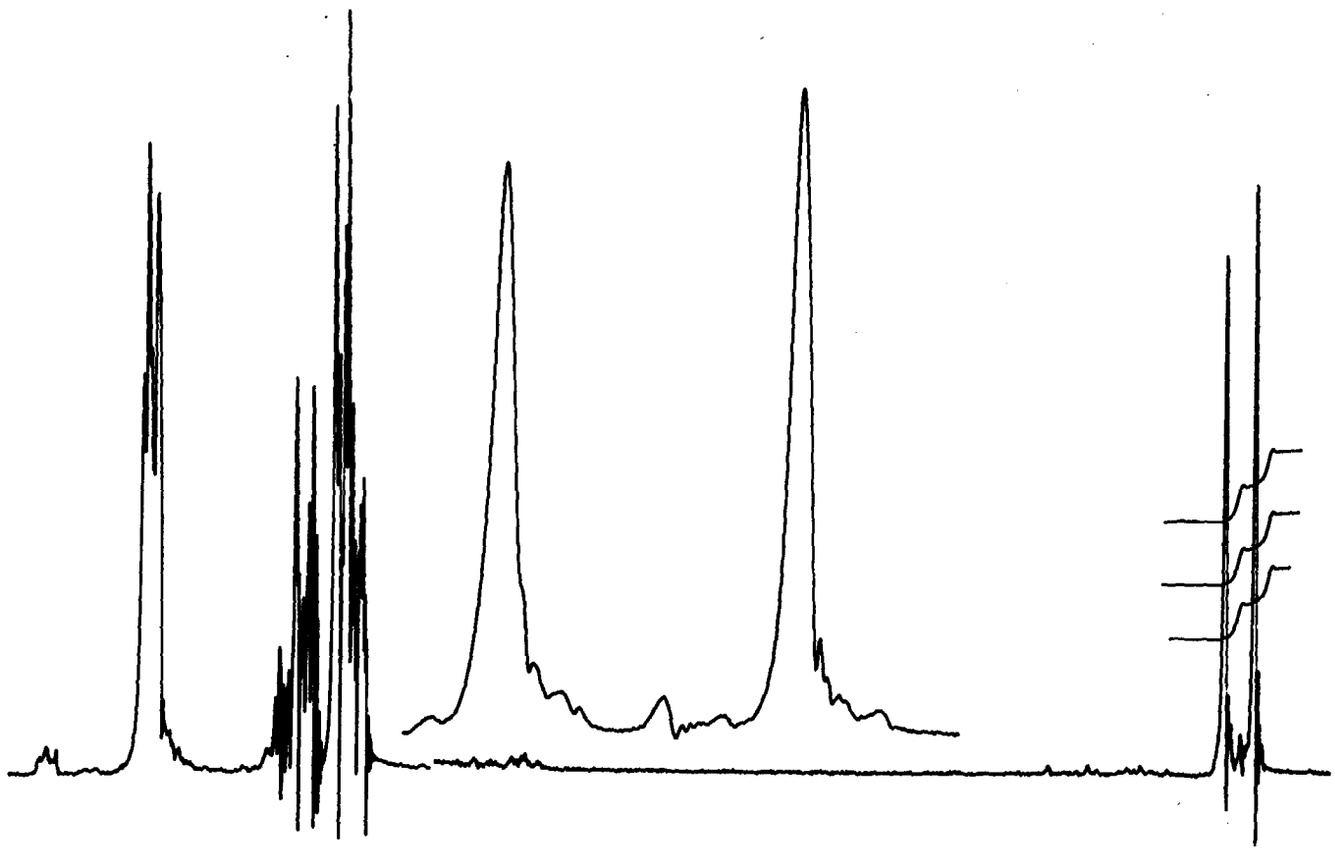

Figure 33. H-NMR spectrum of polymerization of POLYSAC-5 by HRTTT process. Aliquot No. 5.

*U.S.Government Printing Office: 1980 — 657-084/554